Supporting Information

Heteroarene Phosphinylalkylation via a Catalytic, Polarity-Reversing Radical Cascade

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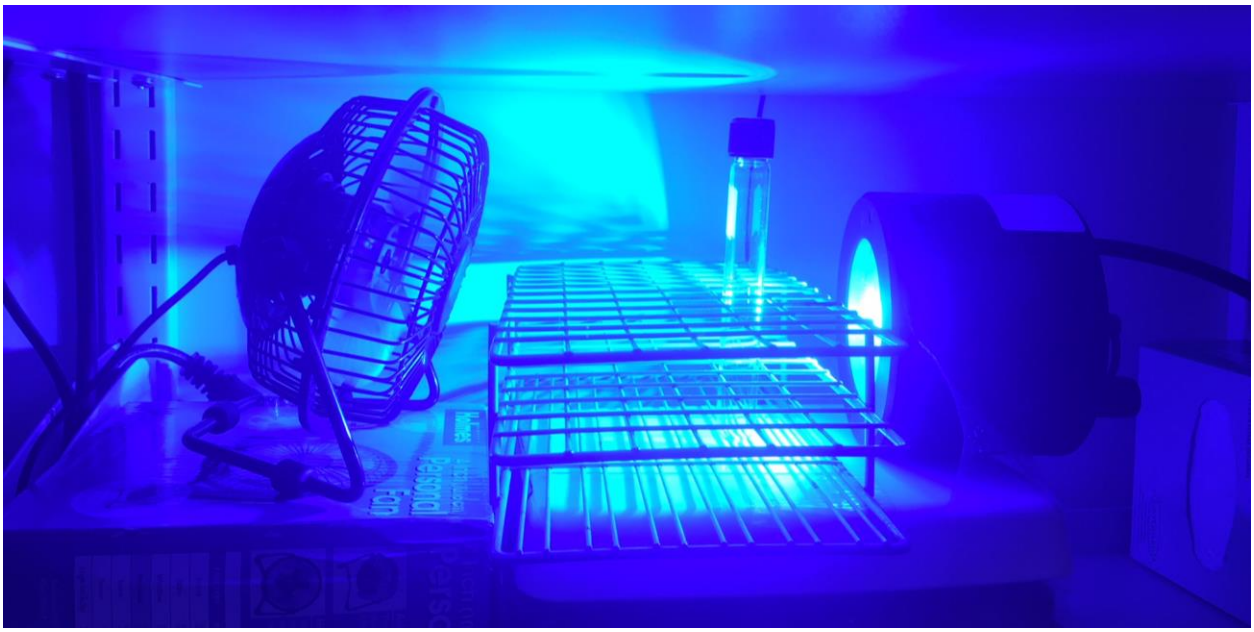
I. General Information

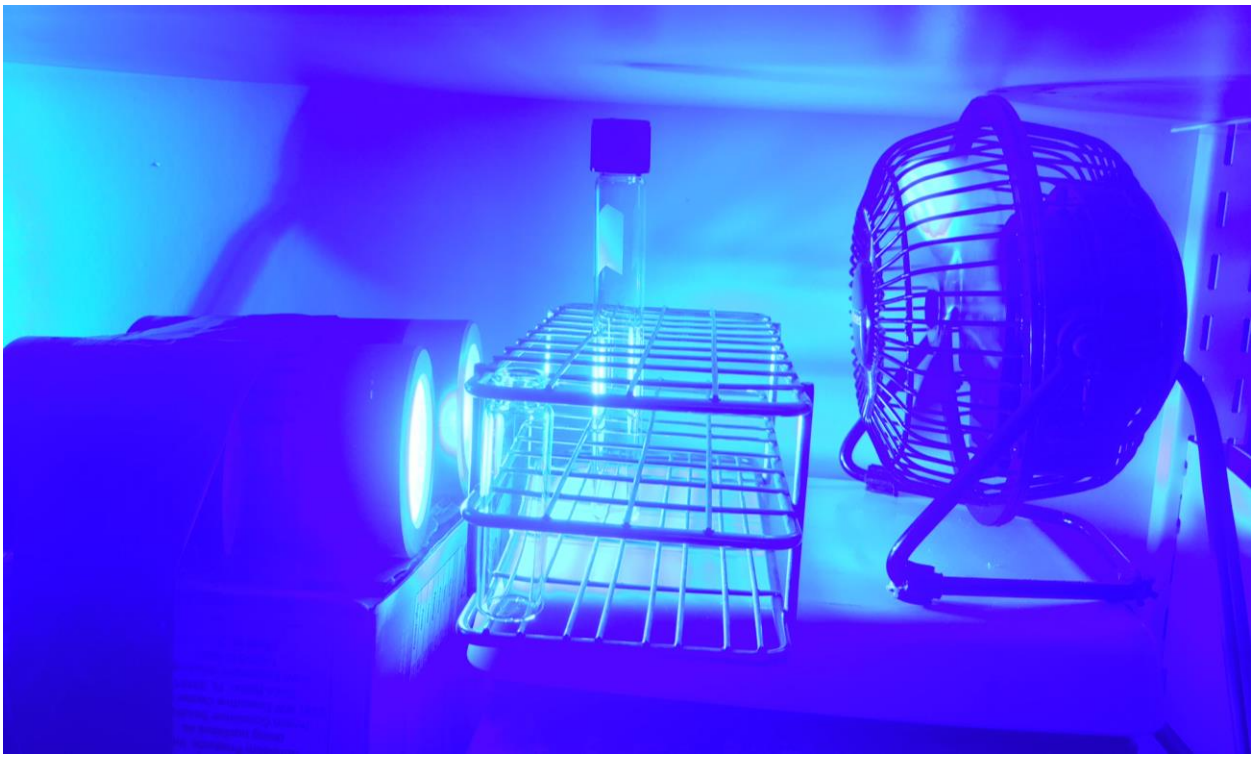
All chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, TCI, or ChemImplex. Reagents were dried under high vacuum before use. Solvents were purified in the following manner. Acetonitrile and amine bases were distilled over calcium hydride. CH_2Cl_2, THF, Et_2O, PhMe, and DMF were degassed with N_2 and dried by passing through columns containing alumina, copper, or molecular sieves. Flash column chromatography, or preparative thin-layer chromatography, was performed with Silicycle F60 (230-400 mesh) silica gel (unless otherwise stated). Thin layer chromatography (TLC) analyses were performed using EMD 60 F254 TLC plates and visualized by fluorescence quenching or $KMnO_4$ stain. All yields are averages of at least two experimental runs.

Nuclear magnetic resonance (NMR) spectra (^1H, ^{19}F, ^{13}C) were recorded using either a Bruker AVIII 400 or AVIII 600 MHz NMR spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in parts per million and referenced to residual $CHCl_3$ signals in $CDCl_3$ (^1H: δ 7.26; ^{13}C: δ 77.16). ^{31}P NMR chemical shifts are reported in parts per million and referenced to phosphoric acid as an external sample (δ 0.00). ^1H NMR data are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, b = broad, ap = apparent), coupling constant (Hz), relative integral. Data for ^{13}C and ^{31}P NMR are reported in terms of chemical shift and multiplicity where appropriate. High-resolution Mass Spectrometry (HRMS) data were obtained using Bruker MicrOTOF (ESI). Infrared (IR) spectra were recorded using a Thermo Fisher Nicolet iS10 FT-IR and are reported in terms of frequency of absorption (cm^{-1}). Melting points were determined using an Electrotherman IA9000.

Photochemical reactions were performed by placing reaction vessel approximately 5.0 cm apart from one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue). See photographs of the set-ups below.



Single lamp, 90W Kessil A360WE tuna blue setup.



Dual lamp, 45W Kessil A160WE tuna blue setup.

II. General Procedures

General Procedure 1 (GP1) – Synthesis of Pyridiniums (modified Herzon procedure[1])

To a 20-mL borosilicate vial with a magnetic stirbar was added pyridine N-oxide (20 mmol, 1 equiv). Next, the vial was evacuated 3x, and placed under N_2 atmosphere while covered with a cap and septa. Next, dimethyl sulfate was added via syringe (2.1 mL, 22 mmol, 1.05 equiv). The vial was then vortexed for approximately one minute, and then placed on a heating block set to the appropriate temperature and allowed to stir overnight. When finished, the reaction was removed from the heating block and 3 mL of anhydrous acetone was added via syringe. The vial was vortexed and allowed to cool to room temperature – afterwards, product crystals began to form. The product was filtered and washed with acetone, then placed on high vacuum overnight.

Notes:

1. Some specimens did not crystalize but instead remained dissolved in acetone. These specimens were only able to be crystalized by dropping the resulting acetone mixture into 150 mL of diethyl ether or hexanes, and allowing to stir overnight before decanting off of the organic solution. The remaining solid or slurry was dissolved in dichloromethane, then condensed and placed under high vacuum overnight.
2. Some specimens required multiple extractions with acetone in order to separate out impurities. For these specimens, the target molecule was poorly soluble in acetone, while the impurities were insoluble. Initially, the first 5 acetone extractions (~2 mL each) were disposed of, then remaining material was continuously extracted with acetone (at least 10x, ~3 mL each extraction). The remaining acetone layers were combined and condensed down, then placed on high vacuum overnight to yield the purified target molecule.
3. Methyl sulfate pyridiniums are exceptionally hygroscopic. Once products were isolated and dried, they were kept in a glovebox under N_2 atmosphere.
4. All reactions run at temperatures higher than 60°C usually gave poorer results. Since reactions are exothermic, it is recommended that lower temperatures (40-60°C) and longer reaction times be taken.

General Procedure 2 (GP2) – Anion Metathesis of Pyridinium Iodides

1-methoxypyridin-1-ium iodides (3 mmol, 1 equiv) and silver salt of choice (mesylate, triflate, or hexafluorophosphate; 3 mmol, 1 equiv) were added to a 8-mL vial equipped with a magnetic stir bar. The vial was capped and evacuated 3x then backfilled with N_2. 3 mL of DCM was added, and the reaction was allowed to stir at room temperature overnight. A yellowish precipitate began to form within 5 minutes. The next day, the precipitate was filtered and washed with DCM, the organic eluent was collected and condensed, then placed on high vacuum overnight to give the target molecule as solid crystals.

General Procedure 3 (GP3)– Three-Component Phosphorylation of Phenanthridine

To a 20-mL borosilicate vial with a magnetic stirbar was added phenanthridine (0.0179 g, 0.1 mmol), diphenyl phosphine oxide (0.0404 g, 0.2 mmol, 2 equiv), and $Ir(ppy)_2(dtbbpy)PF_6$ (0.0009 g, 0.001 mmol, 0.01 equiv), followed by DMSO (1 mL). Next, trifluoroacetic acid (9.2 µL, 0.12 mmol, 1.2 equiv), DI water (10 µL, 0.55 mmol, 5.5 equiv), and alkene (0.2 mmol, 2 equiv) were added. The vial was then capped, vortexed for approximately one minute, and then placed on a stir plate directly in front of a blue LED (see setup above). The reaction vial was then irradiated with one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue) approximately 6 cm away (for quinolines) or 8 cm away (for isoquinolines) from the light source. The reaction temperature was approximately 25˚C, with a fan used to assist cooling. After 12 hours, the reaction was quenched by pipetting into an aqueous solution of sodium bicarbonate (40 mL of DI water & 10 mL of saturated sodium bicarbonate), extracted with 10 mL CH_2Cl_2 (×3), and the combined organic layers were dried over Na_2SO_4, and then condensed under reduced pressures. An internal standard (isopropyl acetate, dibromomethane, or mesitylene) was added to the crude material and yields were determined by ^1H NMR analysis of the crude mixture with deuterated chloroform. The crude mixture was then purified by silica preparatory plate (100% DCM, followed by 1/99 methanol/DCM). The product band was shaved off of the plate, then run through a short silica plug with 5/95 methanol/DCM. The collected eluent was then condensed and next purified by alumina preparatory plate (100% DCM, followed by 0.5/99.5 methanol/DCM). The product band was shaved off of the plate, then run through a short silica plug with 5/95 methanol/DCM. The eluent was condensed, then transferred to an alumina column. The column was flushed with 100 mL of hexanes, 100 mL of DCM, and then fractions were

collected with 100 mL of a 5/95, methanol/DCM gradient. The fractions were condensed and then dried on high vacuum overnight.

Notes:

1. Diphenylphosphine oxide is very hygroscopic. It is recommended that this compound be stored in a glovebox permanently. This material should also be massed in the glovebox to ensure quantitative values.
2. The addition of water may be mitigated on especially humid days.
3. Quinoline species placed 6 cm away from light source tended to give better results than those placed too close or too far away. Isoquinoline species yielded better results at 8 cm away from the light source.

General Procedure 4 (GP4) – Three-Component Phosphorylation of Pyridiniums

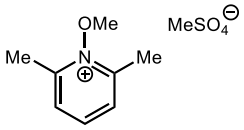
To a 20-mL borosilicate vial with a magnetic stirbar was added pyridinium (0.1 mmol), diphenyl phosphine oxide (0.0404 g, 0.2 mmol, 2 equiv), $Ir(ppy)_2(dtbbpy)PF_6$ (0.0009 g, 0.001 mmol, 0.01 equiv), followed by DMSO (1 mL). Next, Na_2CO_3 (0.0138 g, 0.1 mmol, 1 equiv), DI water (10 µL, 0.55 mmol, 5.5 equiv), and ethyl vinyl ether (19 µL, 0.2 mmol, 2 equiv) were added. The vial was then capped, vortexed for approximately one minute, and then placed on a stir plate next to a blue LED (see setup above). The reaction vial was then irradiated with one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue) at approximately 6 cm away from the light source. The reaction temperature was approximately 25˚C, with a fan used to help with cooling. After 12 hours, the reaction was quenched by pipetting into an aqueous solution of sodium bicarbonate (40 mL of DI water & 10 mL of saturated sodium bicarbonate), extracted with 10 mL CH_2Cl_2 (×3), and the combined organic layers were dried over Na_2SO_4. An internal standard (isopropyl acetate, dibromomethane, or mesitylene) was added to the crude material and yields were determined by ^1H NMR analysis of the crude mixture. The crude mixture was then purified by silica preparatory plate (100% DCM, followed by 1/99 methanol/DCM). The product band was shaved off of the plate, then run through a short silica plug with 5/95 methanol/DCM. The collected eluent was then condensed and next purified by alumina preparatory plate (100% DCM, followed by 0.5/99.5 methanol/DCM). The product band was shaved off of the plate, then run through a short silica plug with 5/95 methanol/DCM. The eluent was condensed, then transferred to an alumina column. The column was flushed with 100

mL of hexanes, 100 mL of DCM, and then fractions were collected with 100 mL of a 5/95, methanol/DCM gradient. The fractions were condensed and then dried on high vacuum overnight.

Notes:

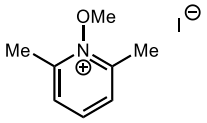
1. Diphenylphosphine oxide is very hygroscopic. It is recommended that this compound be stored in a glovebox permanently. This material should also be massed in the glovebox to ensure quantitative values.
2. All pyridiniums were exceptionally hygroscopic. It is recommended that these compounds be stored in a glovebox permanently. These compounds should also be massed in the glovebox to ensure quantitative values.
3. The addition of water may be mitigated on especially humid days.

III. Synthesis of Starting Materials



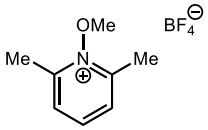
1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate

2,6-dimethylpyridine N-oxide (1.23 g, 10 mmol) was subjected to **GP1** at 40°C. After filtration and drying, the pyridinium was isolated as a white crystal (1.97 g, 79%). Spectra matches literature values.[1]



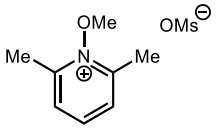
1-methoxy-2,6-dimethylpyridin-1-ium iodide

Prepared according to Herzon's method (76%). Spectra matches literature values.[1]



1-methoxy-2,6-dimethylpyridin-1-ium tetrafluoroborate

Prepared according to Herzon's method (52%). Spectra matches literature values.[1]



1-methoxy-2,6-dimethylpyridin-1-ium methanesulfonate

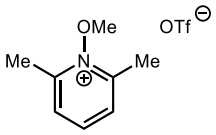
1-methoxy-2,6-dimethylpyridin-1-ium iodide (0.80 g, 3 mmol) and silver mesylate (0.61 g, 3 mmol) were subjected to **GP2**. After filtration and drying, the pyridinium was isolated as a white crystal (0.33 g, 47%).

^{1}H NMR (400 MHz, d-DMSO): δ = 8.22 (t, *J* = 7.9 Hz, 1H); 7.81 (d, *J* = 7.9 Hz, 2H); 4.52 (s, 3H), 2.96 (s, 6H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, d-DMSO): δ = 153.7; 143.9; 128.8; 67.6; 39.5; 18.1.

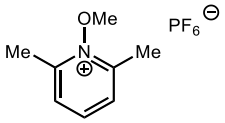
HRMS (ESI-TOF) m/z: calc'd for $C_8H_{12}NO$ 138.0913, found 138.0913.

IR (film) cm^{-1}: 3392, 2360, 2158, 1618, 1497,1171, 1042, 951, 776.



1-methoxy-2,6-dimethylpyridin-1-ium triflate

1-methoxy-2,6-dimethylpyridin-1-ium iodide (0.80 g, 3 mmol) and silver triflate (0.77 g, 3 mmol) were subjected to **GP2**. After filtration and drying, the pyridinium was isolated as a white crystal (0.84 g, 97%). Spectra matches literature values.[1]



1-methoxy-2,6-dimethylpyridin-1-ium hexafluorophosphate (V)

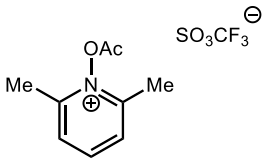
1-methoxy-2,6-dimethylpyridin-1-ium iodide (1.61 g, 6 mmol) and silver hexafluorophosphate (V) (1.59 g, 6.3 mmol) and 6 mL of DCM were subjected to **GP2**. After filtration and drying, the pyridinium was isolated as a white powdery crystal (0.79 g, 46%).

^{1}H NMR (400 MHz, d-DMSO): δ = 8.37 (t, *J* = 7.9 Hz, 1H); 7.97 (d, *J* = 7.9 Hz, 2H); 4.30 (s, 3H), 2.83 (s, 6H).

^{13}C NMR (100 MHz, d-DMSO): δ = 153.3; 143.9; 128.0; 66.9; 17.0.

HRMS (ESI-TOF) m/z: calc'd for $C_8H_{12}NO$ 138.0913, found 138.0907.

IR (film) cm^{-1}: 3381, 2359, 2341, 1653, 1047, 1023, 990, 824, 762.



1-acetoxy-2,6-dimethylpyridin-1-ium trifluoromethansulfonate

2,6-dimethylpyridine N-oxide (0.92 g, 7.5 mmol) was dissolved in 10 mL of methylene chloride and cooled to 0°C in an ice bath while under nitrogen atmosphere. Acetyl chloride (0.65 mL, 8.25 mmol) was slowly added via syringe, and contents were allowed to warm up to room temperature while reaction proceeded overnight. The contents were condensed under reduced pressure and then 5 mL of anhydrous acetone/hexanes (1:1) was added to precipitate our the acetoxy chloride salt, which was then filtered, collected, and dried over high vacuum overnight (1.25 g, 62%). The 1-acetoxy-2,6-dimethylpyridin-1-ium chloride salt (1.0 g, 4.95 mmol) and silver trifluoromethane

sulfonate (1.06 g, 5.2 mmol) were then dissolved in 5 mL of methylene chloride and subjected to **GP2**. After filtration and drying, the pyridinium was recrystallized in ethyl acetate several times and then isolated as a white crystal (0.09 g, 6%).

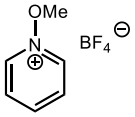
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, *J* = 7.9 Hz, 1H); 7.91 (d, *J* = 7.9 Hz, 2H); 2.78 (s, 6H), 2.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5; 153.8; 145.8; 128.5; 126.4; 18.6; 17.7.

^{19}F NMR (377 MHz, $CDCl_3$): δ = -78.37.

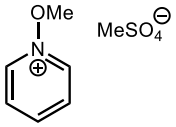
HRMS (ESI-TOF) m/z: calc'd for $C_9H_{12}NO_2$ 166.0863, found 166.0866.

IR (film) cm^{-1}: 1827, 1617, 1592, 1497, 1375, 1252, 1223, 1152, 1122, 1091, 1027, 1001.



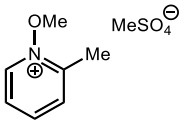
1-methoxypyridin-1-ium tetrafluoroborate

Prepared according to Gould's method, then purified by alumina column (0.5/99.5, methanol/DCM, 3%). Spectra matches literature values.[2]



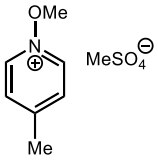
1-methoxypyridin-1-ium methyl sulfate.

Prepared according to Herzon's method, though modified to a lower temperature (40°C) and allowed to react for only 2 hours. Spectra matches literature values.[1]



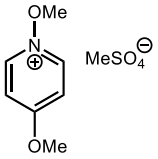
1-methoxy-2-methylpyridin-1-ium methyl sulfate

Prepared according to Herzon's method (30%). Spectra matches literature values.[1]



1-methoxy-4-methylpyridin-1-ium methyl sulfate

Prepared according to Herzon's method (65%). Spectra matches literature values.[1]



1,4-dimethoxypyridin-1-ium methyl sulfate

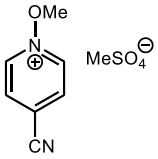
4-methoxypyridine N-oxide (0.19 g, 1.5 mmol) was subjected to **GP1** at 60°C. When completed, contents were issolved in acetone, then slowly added to diethyl ether. Decanted off ether, and white slurry remained. Dissolved slurry in DCM, transferred and condensed, then placed on high vacuum overnight. The pyridinium was isolated as a light brown oil (0.27 g, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.09-9.02 (m, 2H); 7.64-7.58 (m, 2H); 4.42 (d, *J* = 0.6 Hz, 3H); 4.16 (d, *J* = 0.5 Hz, 3H); 3.74 (d, *J* = 0.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7; 142.5; 114.9; 69.9; 58.8; 54.6.

HRMS (ESI-TOF) m/z: calc'd for $C_7H_{10}NO_2$ 140.0706, found 140.0705

IR (film) cm^{-1}: 3465, 3124, 3054, 2952, 2361, 1627, 1572, 1508, 1442, 1314, 1213, 1059, 999, 951, 851, 747.



4-cyano-1-methoxypyridin-1-ium methyl sulfate

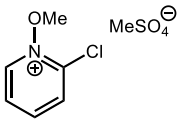
4-cyanopyridine N-oxide (1.04 g, 8.7 mmol) was subjected to **GP1** at 40°C. When completed, contents were extracted (10x) with DCM. The DCM layers were discarded. The remaining oil was then placed on high vacuum overnight. The pyridinium was isolated as a rose-colored oil (1.21 g, 57%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81-9.76 (m, 2H); 8.88-8.84 (m, 2H); 4.49 (s, 3H); 3.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1; 132.4; 125.9; 114.4; 69.5; 52.7.

HRMS (ESI-TOF) m/z: calc'd for $C_7H_7N_2O$ 135.0553, found 135.0546

IR (film) cm^{-1}: 3438, 3100, 3082, 3051, 2359, 2342, 2230, 1610, 1479, 1446, 1279, 1173, 1032, 852, 747, 713.



2-chloro-1-methoxypyridin-1-ium methyl sulfate

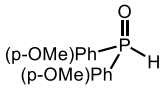
2-chloropyridine N-oxide (1.3 g, 10 mmol) was subjected to **GP1** at 40°C. When completed, contents were dissolved in 50:50 DCM:acetone mixture, then added (dropwise) to diethyl ether solution and allowed to stir overnight. The ether solution was decanted off, and remaining solid was then collected and placed on high vacuum overnight. The pyridinium was isolated as a light orange solid (1.41 g, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70 (dd, *J* = 6.6, 1.6 Hz, 1H); 8.59 (td, *J* = 12.0, 1.1 Hz, 1H); 8.35-8.29 (m, 1H); 8.13 (dd, *J* = 8.2, 1.7 Hz, 1H); 4.61 (s, 3H); 3.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7; 145.2; 144.3; 130.6; 129.2; 70.3; 54.6.

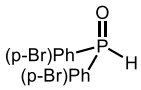
HRMS (ESI-TOF) m/z: calc'd for C_6H_7ClNO 144.0211, found 144.0204.

IR (film) cm^{-1}: 3421, 3105, 2947, 2360, 2343, 1648, 1576, 1535, 1473, 1424, 1220, 1059, 1006, 760.



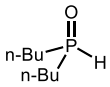
bis(4-methoxyphenyl)phosphine oxide

Prepared according to Busacca's method (61%). Spectra matches literature values.[3]



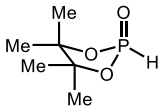
bis(4-bromophenyl)phosphine oxide

Prepared according to Wang's method. Spectra matches literature values.[4]



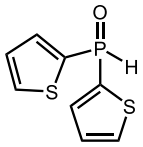
dibutylphosphine oxide

Prepared according to Busacca's method (60%). Spectra matches literature values.[3]



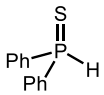
4,4,5,5-tetramethyl-1,3,2-dioxophospholane 2-oxide

Prepared according to Munoz' method (41%). Spectra matches literature values.[5]



di(thiophen-2-yl)phosphine oxide

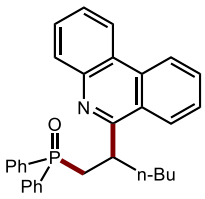
Prepared according to Mathey's method (48%). Spectra matches literature values.[6]



diphenylphosphine sulfide

Prepared according to Koenig's method (64%). Spectra matches literature values.[7]

IV. Synthesis of Products



(2-(phenanthridin-6-yl)hexyl)diphenylphosphine oxide (1)

1-hexene (25 uL, 0.2 mmol) was subjected to **GP3** (reaction can be carried out with and without Iridium catalyst for similar yields). Isopropyl acetate was used as an internal standard and ^{1}H NMR yield was determined to be 80%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.43 (silica, 25/75, acetonitrile/DCM)

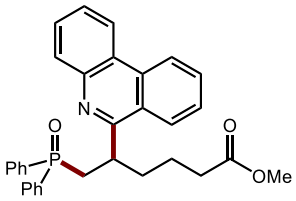
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, 8.1 Hz, 1H); 8.39 (d, *J* = 8.3 Hz, 1H); 8.28 (d, *J* = 8.3 Hz, 1H); 7.99 (d, 8.1 Hz, 1H); 7.80-7.71 (m, 3H); 7.68-7.55 (m, 3H); 7.48-7.40 (m, 3H); 7.20-7.15 (m, 2H); 6.75 (t, *J* = 7.5 Hz, 1H); 6.57 (td, *J* = 11.5, 2.6 Hz, 2H); 4.50-4.43 (m, 1H); 3.60-3.54 (m, 1H); 2.75 (td, *J* = 22.7, 3.2 Hz, 1H); 2.13-2.06 (m, 1H); 1.92-1.85 (m, 1H, overlap); 1.30-1.17 (m, 3H, overlap); 1.13-1.05 (m, 1H); 0.74 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.4 (d, *J* = 3.3 Hz); 143.6; 134.9 (d, *J* = 97.9 Hz); 132.7; 132.0 (d, *J* = 96.8 Hz); 131.6 (d, *J* = 2.2 Hz); 130.6 (d, *J* = 8.8 Hz); 130.3 (d, *J* = 2.2 Hz); 130.1; 129.7; 128.6 (d, *J* = 11.0 Hz); 128.2; 127.2 (d, *J* = 11.0, overlap); 127.2 (s, overlap); 126.3; 126.0; 125.6; 123.6; 122.1; 121.8; 37.9 (d, *J* = 12.1 Hz); 35.5 (d, *J* = 70.4 Hz); 35.02(s, broad); 29.6; 22.8; 13.9.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 30.54.

HRMS (ESI-TOF) m/z: calc'd for $C_{31}H_{31}NOP$ (M+H) 464.2138, found 464.2116.

IR (film) cm^{-1}: 3408, 3057, 2954, 2926, 2856, 1437, 1180, 1118, 760, 743, 695.



methyl-6-(diphenylphosphoryl)-5-(phenanthridine-6-yl)hexanoate (2)

Methyl hex-5-enolate (0.0256 g, 0.2 mmol) was subjected to **GP3**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 59%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.23 (silica, 25/75, acetonitrile/DCM)

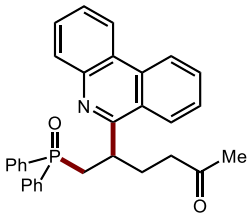
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.3 Hz, 1H); 8.40 (dd, *J* = 8.1, 1.4 Hz, 1H); 8.25 (d, *J* = 8.3 Hz, 1H); 7.98 (dd, *J* = 8.1, 1.1 Hz, 1H); 7.79-7.72 (m, 3H); 7.69-7.55 (m, 3H); 7.49-7.39 (m, 3H); 7.23-7.15 (m, 2H); 6.82-6.75 (m, 1H); 6.65-6.57 (m, 2H); 4.54-4.42 (m, 1H); 3.55 (s, 3H, overlap); 3.55-3.46 (m, 1H, overlap); 2.73 (td, *J* = 22.6, 3.7 Hz, 1H); 2.20 (t, *J* = 7.5 Hz, 2H, overlap); 2.20-2.12 (m, 1H, overlap); 1.99-1.88 (m, 1H); 1.67-1.58 (m, 1H); 1.49-1.37 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.7; 162.7 (d, *J* = 4.3 Hz); 143.7; 135.1 (d, *J* = 98.0 Hz); 132.9; 132.3 (d, *J* = 97.9 Hz); 131.6 (d, *J* = 2.2 Hz); 130.8 (d, *J* = 9.9 Hz, overlap); 130.7 (d, *J* = 8.8 Hz, overlap); 130.4 (d, *J* = 2.2 Hz); 130.2; 129.9; 128.7 (d, *J* = 12.1 Hz); 128.3; 127.4 (d, *J* = 12.1 Hz, overlap); 127.4 (s, overlap); 126.5; 126.0; 125.6; 123.7; 122.2; 121.8; 51.4; 37.2 (d, *J* = 10.9 Hz); 35.6 (d, *J* = 71.5 Hz); 35.1 (s, broad); 34.2; 22.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.23.

HRMS (ESI-TOF) m/z: calc'd for $C_{32}H_{31}NO_3P$ (M+H) 508.2036, found 508.2021.

IR (film) cm^{-1}: 3057, 2995, 2928, 2854, 2360, 1734, 1605, 1437, 1393, 1364, 1240, 1201, 1174, 1119, 860, 827, 719.



6-(diphenylphosphoryl)-5-(phenanthridine-6-yl)hexan-2-one (3)

5-Hexen-2-one (23 μL, 0.2 mmol) was subjected to **GP3**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 60%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.28 (silica, 25/75, acetonitrile/DCM)

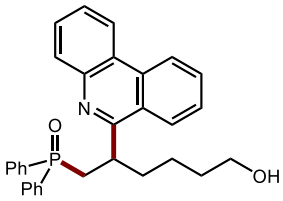
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.4Hz, 1H); 8.41 (d, *J* = 8.3 Hz, 1H); 8.25 (d, *J* = 8.4 Hz, 1H); 7.99 (d, *J* = 8.3 Hz, 1H); 7.79-7.73 (m, 3H); 7.69-7.57 (m, 3H); 7.49-7.40 (m, 3H); 7.23-7.18 (m, 2H); 6.81 (td, *J* = 11.5, 2.6 Hz, 2H); 4.52-4.44 (m, 1H); 3.57-3.50 (m, 1H); 2.72 (td, *J* = 22.7, 3.7 Hz, 1H); 2.46-2.28 (m, 3H); 2.22-2.16 (m, 1H); 1.96 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 208.2; 162.3 (d, *J* = 5.0 Hz); 143.5; 134.6 (d, *J* = 97.9 Hz); 132.8; 131.8 (d, *J* = 97.8); 131.7 (d, *J* = 2.2 Hz); 130.7 (d, *J* = 9.9 Hz); 130.6 (d, *J* = 9.9 Hz); 130.5 (d, *J* = 2.2 Hz); 130.4; 129.8; 128.7 (d, *J* = 11.0 Hz); 128.3; 127.4 (s, overlap); 127.4 (d, *J* = 12.2 Hz, overlap); 126.6; 125.9; 125.4; 123.6; 122.2; 121.8; 41.1; 35.4 (d, *J* = 70.8 Hz); 34.3 (s, broad); 31.4 (d, *J* = 11.0 Hz); 29.9.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 30.33.

HRMS (ESI-TOF) m/z: calc'd for $C_{31}H_{29}NO_2P$ (M+H) 478.1930, found 478.1944.

IR (film) cm^{-1}: 3057, 2922, 2361, 2344, 1710, 1487, 1437, 1177, 1118, 913, 745, 696.



(6-hydroxy-2-(phenanthridin-6-yl)hexyl)diphenylphosphine oxide (4)

5-Hexen-1-ol (24 μL, 0.2 mmol) was subjected to **GP3**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 70%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.28 (silica, 25/75, acetonitrile/DCM)

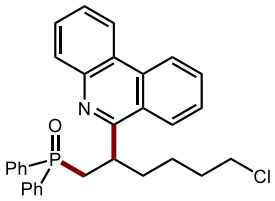
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 1H); 8.38 (d, *J* = 8.3 Hz, 1H); 8.19 (d, *J* = 7.0 Hz, 1H); 7.99 (s, 1H); 7.77-7.69 (m, 3H); 7.64 (t, *J* = 7.5 Hz, 1H); 7.59-7.53 (m, 2H); 7.45-7.36 (m, 3H); 7.23-7.19 (m, 2H); 6.80 (t, *J* = 7.2 Hz, 1H); 6.67-6.61 (m, 2H); 4.43 (s, 1H); 3.54-3.41 (m, 3H); 2.78 (td, *J* = 15.1, 3.9 Hz, 1H); 2.38 (bs, 1H); 2.19-2.09 (m, 1H); 1.94-1.85 (m, 1H); 1.46 (quintet, *J* = 7.0, 2H); 1.39-1.31 (m, 1H); 1.28-1.19 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.1 (d, *J* = 2.2 Hz); 143.5; 134.6 (d, *J* = 99.0 Hz); 132.8; 131.8 (d, *J* = 96.8 Hz); 131.7 (d, *J* = 2.2 Hz); 130.7 (d, *J* = 9.9 Hz); 130.6 (d, *J* = 9.9 Hz); 130.5 (d, *J* = 2.2 Hz); 130.3; 129.7; 128.7 (d, *J* = 11.0 Hz); 128.4; 127.4 (d, *J* = 11.0, overlap); 127.4 (s, overlap); 126.5; 125.9; 125.4; 123.6; 122.2; 121.8; 62.4; 37.1 (d, *J* = 9.9 Hz); 35.1 (d, *J* = 70.4 Hz); 35.0 (s, broad); 32.6; 23.4.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 31.10.

HRMS (ESI-TOF) m/z: calc'd for $C_{31}H_{31}NO_2P$ (M+H) 480.2087, found 480.2044.

IR (film) cm^{-1}: 3310, 3058, 2931, 2858, 2360, 2225, 1572, 1437, 1172, 1118, 908, 726.



(6-chloro-2-(phenanthridin-6-yl)hexyl)diphenylphosphine oxide (5)

6-chloro-1-hexene (24 μL, 0.2 mmol) was subjected to **GP3**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 76%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.57 (silica, 25/75, acetonitrile/DCM).

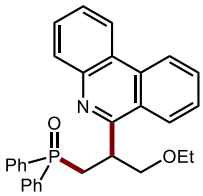
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.3 Hz, 1H); 8.45 (d, *J* = 7.9 Hz, 1H); 8.29 (d, *J* = 8.4 Hz, 1H); 8.03 (dd, *J* = 8.1, 0.8 Hz, 1H); 7.84-7.77 (m, 3H); 7.73-7.61 (m, 3H); 7.54-7.45 (m, 3H); 7.27-7.22 (m, 2H); 6.86-6.82 (m, 1H); 6.67 (td, *J* = 11.5, 2.6 Hz, 2H); 4.55-4.47 (m, 1H); 3.56-3.50 (m, 1H); 3.44-3.36 (m, 2H); 2.79 (td, *J* = 22.4, 3.9 Hz, 1H); 2.24-2.17 (m, 1H); 2.00-1.93 (m, 1H); 1.73-1.64 (m, 2H); 1.50-1.42 (m, 1H, overlap); 1.30-1.24 (m, 1H, overlap).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.9 (d, *J* = 4.4 Hz); 143.6; 134.7 (d, *J* = 97.9 Hz); 132.8; 131.8 (d, *J* = 97.9 Hz); 131.7 (d, *J* = 2.2 Hz); 130.7 (d, *J* = 9.9 Hz); 130.6 (d, *J* = 8.8 Hz); 130.4 (d, *J* = 3.3 Hz); 130.3; 129.8; 128.7 (d, *J* = 12.1 Hz); 128.3; 127.4; 127.4 (d, *J* = 12.1 Hz); 126.5; 125.9; 125.5; 123.6; 122.2; 121.8; 44.7; 37.0 (d, *J* = 9.9 Hz); 35.6 (d, *J* = 70.4 Hz); 34.9 (s, broad); 32.8; 24.7.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 30.42.

HRMS (ESI-TOF) m/z: calc'd for $C_{31}H_{31}ClNOP$ (M+H) 498.1748, found 498.1734.

IR (film) cm^{-1}: 3057, 2928, 2858, 2363, 2345, 1437, 1181, 1118, 913, 745, 696.



(3-ethoxy-2-(phenanthridin-6-yl)propyl)diphenylphosphine oxide (6)

Allyl ethyl ether (23 μL, 0.2 mmol) was subjected to **GP3**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 65%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.30 (silica, 25/75, acetonitrile/DCM)

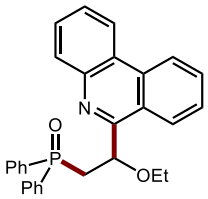
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.8 Hz, 1H); 8.40 (d, *J* = 8.3 Hz, 1H); 8.30 (d, *J* = 8.4 Hz, 1H); 7.98 (dd, *J* = 8.1, 1.1 Hz, 1H); 7.79-7.73 (m, 3H); 7.67-7.56 (m, 3H); 7.46-7.38 (m, 3H); 7.26-7.22 (m, 2H, overlap); 6.82-6.79 (m, 1H); 6.64 (td, *J* = 11.7, 2.7 Hz, 2H); 4.74-4.67 (m, 1H); 3.88-3.81 (m, 2H); 3.56-3.50 (m, 1H); 3.48-3.42 (m, 2H); 3.01 (td, *J* = 22.7, 3.1 Hz, 1H); 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.7 (d, *J* = 2.3 Hz); 143.4; 134.5 (d, *J* = 98.2 Hz); 132.8; 132.1 (d, *J* = 97.9 Hz); 131.6 (d, *J* = 2.2 Hz); 130.8 (d, *J* = 8.8 Hz); 130.7 (d, *J* = 8.8 Hz); 130.4 (d, *J* = 3.3 Hz); 130.2; 129.8; 128.6 (d, *J* = 12.1 Hz); 128.2; 127.4; 127.3 (d, *J* = 9.9 Hz); 126.5; 126.2; 125.6; 123.7; 122.0; 121.8; 75.0 (d, *J* = 13.2 Hz); 66.5; 36.0 (d, *J* = 2.2 Hz); 31.7 (d, *J* = 71.5 Hz); 15.2.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 31.18.

HRMS (ESI-TOF) m/z: calc'd for $C_{30}H_{29}NO_2P$ (M+H) 466.1930, found 466.1923.

IR (film) cm^{-1}: 3057, 2954, 2926, 2856, 1611, 1572, 1487, 1437, 1180, 1118, 1104, 760, 743, 725, 645.



(2-ethoxy-2-(phenanthridin-6-yl)ethyl)diphenylphosphine oxide (7)

Ethyl vinyl ether (19 μL, 0.2 mmol) was subjected to **GP3** without the inclusion of trifluoroacetic acid. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 83%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.18 (silica, 1.5/5/93.5, triethylamine/methanol/DCM)

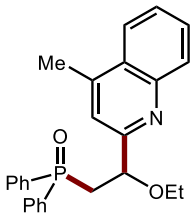
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.2 Hz, 1H); 8.59 (d, *J* = 8.3 Hz, 1H); 8.49 (dd, *J* = 8.1, 1.1 Hz, 1H); 8.13 (dd, *J* = 8.1, 1.1 Hz, 1H); 7.90-7.85 (m, 2H); 7.84-7.80 (m, 1H); 7.72-7.67 (m, 2H); 7.65-7.61 (m, 1H); 7.56-7.48 (m, 3H); 7.48-7.43 (m, 2H); 7.21-7.17 (m, 1H); 7.13-7.08 (m, 2H); 5.86 (ddd, *J* = 9.6, 7.7, 5.3 Hz, 1H); 3.44-3.34 (m, 2H); 3.27 (ddd, *J* = 15.2, 9.7, 7.7 Hz, 1H); 3.15 (ddd, *J* = 15.2, 11.8, 5.3 Hz, 1H); 0.92 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ =159.3 (d, *J* = 8.7 Hz); 143.3; 133.8 (d, *J* = 100.0 Hz); 133.4; 133.1 (d, *J* = 99.9 Hz); 131.6 (d, *J* = 2.2 Hz); 131.2 (d, *J* = 9.4 Hz); 130.7 (d, *J* = 9.3 Hz); 130.6; 130.5; 128.6; 128.5 (d, *J* = 12.0 Hz); 128.2 (d, *J* = 11.8 Hz); 127.5; 127.2; 126.1; 124.5; 124.1; 122.5; 121.9; 75.7 (s, broad); 64.9; 36.4 (d, *J* = 69.8 Hz); 15.1.

^{31}P NMR (243 MHz, $CDCl_3$): δ =29.14.

HRMS (ESI-TOF) m/z: calc'd for $C_{29}H_{27}NO_2P$ (M+H) 452.1774, found 452.1771.

IR (film) cm^{-1}: 3057, 2974, 2925, 1611, 1574, 1437, 1181, 1119, 910, 762, 729.



2-ethoxy-2-(4-methylquinolin-2-yl)ethyl)diphenylphoshpine oxide (8)

Ethyl vinyl ether (19 µL, 0.2 mmol) was subjected to **GP3** without DI H_2O, using 4-methylquinoline (13.5 µL, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 80%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.20 (silica, 5/95, MeOH/DCM).

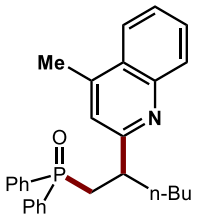
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 8.4, 0.6 Hz, 1H); 7.91 (dd, *J* = 8.4, 0.9 Hz, 1H); 7.86-7.80 (m, 2H); 7.70-7.64 (m, 3H); 7.54-7.40 (m, 4H); 7.33-7.23 (m, 3H, overlap); 7.32 (s, 1H, overlap); 5.04 (td, *J* = 13.0, 5.0 Hz, 1H); 3.39-3.27 (m, 2H); 3.05-2.89 (m, 2H); 2.64 (d, *J* = 0.8 Hz, 3H); 0.94 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (d, *J* = 9.7 Hz); 147.7; 145.2; 133.9 (d, *J* = 100.5 Hz); 133.6 (d, *J* = 99.4 Hz); 131.5 (d, *J* = 2.6 Hz); 131.3 (d, *J* = 2.8 Hz); 131.2 (d, *J* = 9.6 Hz); 130.9 (d, *J* = 9.5 Hz); 130.0; 129.3; 128.4 (d, *J* = 11.9Hz); 128.2 (d, *J* = 11.8 Hz); 127.7; 126.3; 123.7; 119.7; 77.7 (d, *J* = 1.7 Hz, overlap); 65.3; 37.7 (d, *J* = 70.3 Hz); 18.9; 15.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.96.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{26}H_{27}NO_2P$ (M+H) 416.1774, found 416.1759.

IR (film) cm^{-1}: 3055, 2972, 1599, 1562, 1437, 1183, 1118, 998.



(2-(4-methylquinolin-2-yl)hexyl)diphenylphosphine oxide (9)

1-hexene (25 µL, 0.2 mmol) was subjected to **GP3** without DI H_2O, using 4-methylquinoline (13.5 µL, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 41%. Isolation by preparatory plate resulted in a clear oil.

R_f: 0.20 (silica, 5/95, methanol/DCM)

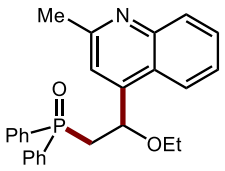
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.2 Hz, 1H); 7.79 (dd, *J* = 8.3, 0.9 Hz, 1H); 7.77-7.70 (m, 2H); 7.62 (t, *J* = 7.5 Hz, 1H); 7.48-7.35 (m, 6H); 7.02-6.95 (m, 1H); 6.92-6.84 (m, 3H); 3.57-3.45 (m, 1H); 3.32-3.21 (m, 1H); 2.63 (td, *J* = 22.4, 3.8 Hz, 1H); 2.46 (s, 3H); 2.03-1.93 (m, 1H); 1.87-1.78 (m, 1H); 1.25-1.17 (m, 3H, overlap); 1.09-1.00 (m, 1H); 0.76 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ =163.3 (d, *J* = 3.7 Hz); 147.9; 143.7; 134.9 (d, *J* = 97.8 Hz); 132.3 (d, *J* = 97.4 Hz); 131.6 (d, *J* = 2.6 Hz); 130.9 (d, *J* = 9.5 Hz); 130.5 (d, *J* = 9.0 Hz, overlap); 130.5 (d, *J* = 1.4 Hz, overlap); 129.6; 128.6 (d, *J* = 11.4 Hz); 127.5 (d, *J* = 11.7 Hz); 127.1; 125.5 (s, overlap); 125.5 (s, overlap); 123.6 (s, overlap); 123.5 (s, overlap); 41.6 (d, *J* = 2.9 Hz); 37.6 (d, *J* = 10.7 Hz); 35.5 (d, *J* = 70.9 Hz); 29.7; 22.7; 18.5; 14.0.

^{31}P NMR (162 MHz, $CDCl_3$): 30.37.

HRMS (ESI-TOF) m/z: calc'd for $C_{28}H_{31}NOP$ (M+H) 428.2138, found 428.2125.

IR (film) cm^{-1}: 3056, 2954, 2926, 2855, 2360, 2342, 1718, 1601, 1560, 1507, 1437, 1184, 1117, 1070, 1027, 997.



(2-ethoxy-2-(2-methylquinolin-4-yl)ethyl)diphenylphosphine oxide (10)

Ethyl vinyl ether (40 µL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using 2-methylquinoline (13.5 µL, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 57%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.30 (silica, 5/95, MeOH/DCM).

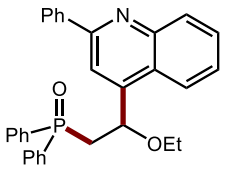
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.3 Hz, 1H); 8.00 (d, *J* = 8.4 Hz, 1H); 7.88-7.83 (m, 2H); 7.66 (t, *J* = 7.6 Hz, 1H); 7.60-7.55 (m, 2H); 7.54-7.47 (m, 4H); 7.41-7.37 (m, 1H); 7.32 (s, 1H, overlap); 7.31-7.28 (m, 2H, overlap); 5.60-5.54 (m, 1H); 3.31-3.26 (m, 1H); 3.24-3.20 (m, 1H); 2.97-2.91 (m, 1H); 2.76-2.70 (m, 1H); 2.67 (s, 3H); 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.8; 148.3; 147.5; 133.4 (d, *J* = 99.6 Hz); 133.3 (d, *J* = 100.9 Hz); 131.7 (d, *J* = 2.0 Hz); 131.5 (d, *J* = 2.3 Hz); 131.1 (d, *J* = 9.6 Hz); 130.3 (d, *J* = 9.3 Hz); 129.5; 129.3; 128.4 (d, *J* = 11.7 Hz); 128.3 (d, *J* = 12.0 Hz); 126.1; 123.9; 123.2; 119.0; 73.1; 65.1; 38.3 (d, *J* = 69.7 Hz); 14.8.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 28.64.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{26}H_{27}NO_2P$ (M+H) 416.1774, found 416.1769.

IR (film) cm^{-1}: 3056, 2974, 1601, 1437, 1181, 1117, 1095.



2-ethoxy-2-(2-phenylquinolin-4-yl)ethyl)diphenylphoshpine oxide (11)

Ethyl vinyl ether (19 µL, 0.2 mmol) was subjected to **GP3** without DI H_2O, using 2-phenylquinoline (0.0205 g, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 58%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.33 (silica, 5/95, MeOH/DCM).

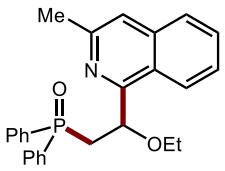
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.1 Hz, 1H); 8.19-8.10 (m, 3H); 7.95 (s, 1H); 7.74-7.68 (m, 1H); 7.63-7.44 (m, 9H); 7.40-7.35 (m, 1H); 7.31-7.26 (m, 2H, overlap); 5.67 (td, *J* = 14.3, 3.4 Hz, 1H); 3.40-3.23 (m, 2H); 3.01 (ddd, *J* = 15.4, 8.8, 6.8 Hz, 1H); 2.80 (ddd, *J* = 15.3, 13.0, 3.5 Hz, 1H); 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3; 148.9; 148.3 (d, *J* = 10.0 Hz); 139.7; 133.4 (d, *J* = 99.8 Hz, overlap); 133.4 (d, *J* = 100.8 Hz, overlap); 131.8 (d, *J* = 2.5 Hz); 131.7 (d, *J* = 2.7 Hz); 131.3 (d, *J* = 9.6 Hz); 130.7; 130.5 (d, *J* = 9.5 Hz); 129.6; 129.5; 128.9; 128.6 (d, *J* = 9.4 Hz, overlap); 128.5 (d, *J* = 9.9 Hz, overlap); 127.7; 126.7; 124.7; 123.3; 116.1; 73.4 (d, *J* = 2.3 Hz); 65.3; 38.6 (d, *J* = 769.6 Hz); 15.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.78.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{31}H_{29}NO_2P$ (M+H) 478.1930, found 478.1990.

IR (film) cm^{-1}: 3057, 2973, 1596, 1551, 1437, 1180, 1116, 907.



(2-ethoxy-2-(3-methylisoquinolin-1-yl)ethyl diphenylphosphine oxide (12)

Ethyl vinyl ether (40 μL, 0.4 mmol) was subjected to **GP3** with 2mL of DMSO and without TFA, using 3-methylisoquinoline (0.0143 g, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 73%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.33 (silica, 5/95, MeOH/DCM).

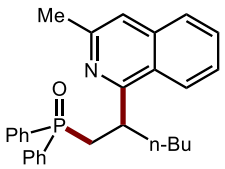
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 8.4 Hz, 1H); 7.88-7.83 (m, 2H); 7.65 (d, *J* = 8.2 Hz, 1H); 7.60-7.56 (m, 1H); 7.55-7.44 (m, 4H); 7.47-7.44 (m, 2H); 7.31-7.27 (m, 1H, overlap); 7.27 (s, 1H, overlap); 7.23-7.18 (m, 2H); 5.76 (ddd, J = 9.2, 7.5, 5.5 Hz, 1H); 3.36-3.27 (m, 2H); 3.22 (ddd, J = 15.1, 10.0, 7.5 Hz, 1H); 3.07 (ddd, J = 15.1, 11.6, 5.5 Hz, 1H); 2.60 (s, 3H); 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.6 (d, *J* = 7.9 Hz); 150.7; 137.5; 133.9 (d, J = 99.8 Hz, overlap); 133.3 (d, J = 98.4 Hz, overlap); 131.6 (d, *J* = 2.3 Hz); 131.3 (d, *J* = 2.3 Hz); 131.7 (d, *J* = 9.2 Hz); 130.7 (d, *J* = 9.6 Hz); 129.9; 128.5 (d, *J* = 11.7 Hz); 128.2 (d, *J* = 12.0 Hz); 126.8; 126.4; 124.9; 124.7; 118.9; 74.7; 64.8; 36.7 (d, *J* = 70.2 Hz); 24.3; 15.2.

^{31}P NMR (243MHz, $CDCl_3$): δ = 28.91.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{26}H_{27}NO_2P$ (M+H) 416.1774, found 416.1765.

IR (film) cm^{-1}: 3054, 2922, 2852, 1437, 1182, 1118, 749, 719, 695.



(2-(3-methylisoquinolin-1-yl)hexyl)diphenylphosphine oxide (13)

1-hexene (19 µL, 0.2 mmol) was subjected to **GP3**, using 3-methylisoquinoline (0.0143 g, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 66%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.20 (silica, 100% Ethyl Acetate).

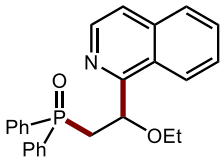
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.4 Hz, 1H); 7.79-7.72 (m, 2H); 7.51-7.38 (m, 6H); 7.24-7.17 (m, 2H); 7.04 (s, 1H); 7.02-6.96 (m, 1H); 6.91-6.84 (m, 2H); 4.40-4.29 (m, 1H); 3.39 (ddd, *J* = 15.0, 9.2, 6.0 Hz, 1H); 2.68 (td, *J* = 22.6, 3.5 Hz, 1H); 2.52 (d, *J* = 0.5 Hz, 3H); 2.03-1.92 (m, 1H); 1.87-1.76 (m, 1H, overlap); 1.24-1.12 (m, 3H, overlap with grease); 1.02-0.92 (m, 1H); 0.73 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (d, *J* = 3.6 Hz); 150.1; 136.9; 134.9 (d, *J* = 97.6 Hz); 132.2 (d, *J* = 97.4 Hz); 131.5 (d, *J* = 2.4 Hz); 130.6 (d, *J* = 9.2 Hz, overlap); 130.5 (d, *J* = 9.3 Hz, overlap); 129.5; 128.6 (d, *J* = 11.6 Hz); 127.4(d, *J* = 11.7 Hz); 126.4; 125.9; 125.5; 125.1; 117.3; 38.3 (d, *J* = 11.4 Hz); 35.5 (d, *J* = 70.8 Hz); 34.6 (d, *J* = 2.6 Hz); 29.6; 24.4; 22.8; 13.9.

^{31}P NMR (162MHz, $CDCl_3$): δ = 30.24.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{28}H_{31}NOP$ (M+H) 428.2138, found 428.2118.

IR (film) cm^{-1}: 3053, 2954, 2923, 2855, 1623, 1591, 1561, 1436, 1413, 1319, 1181, 1117, 1070, 1028, 997, 980, 923.



(2-ethoxy-2-(isoquinolin-1-yl)ethyl)diphenylphosphine oxide (14)

Ethyl vinyl ether (40 µL, 0.4 mmol) was subjected to **GP3** with 2mL of DMSO and without TFA, using isoquinoline (11.75 µL, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 72%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.30 (silica, 5/95, MeOH/DCM).

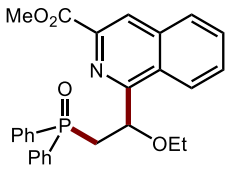
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 8.5 Hz, 1H); 8.45 (d, *J* = 5.6 Hz, 1H); 7.90-7.5 (m, 2H); 7.76 (d, *J* = 8.1 Hz, 1H); 7.65 (t, *J* = 7.5 Hz, 1H); 7.60 (t, J = 7.6 Hz, 1H, overlap); 7.58-7.54 (m, 2H, overlap); 7.52-7.44 (m, 4H); 7.32-7.28 (m, 1H); 7.25-7.21 (m, 2H); 5.83 (td, J = 13.1, 4.7 Hz, 1H); 3.31-3.21 (m, 3H); 2.94 (ddd, J = 15.1, 12.1, 4.5 Hz, 1H); 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5 (d, *J* = 9.0 Hz); 142.1; 136.6; 133.8 (d, *J* = 100.3 Hz); 133.5 (d, *J* = 99.3 Hz); 131.6 (d, *J* = 2.6 Hz); 131.3 (d, *J* = 2.2 Hz); 131.2 (d, *J* = 9.8 Hz); 130.6 (d, *J* = 9.3 Hz); 130.1; 128.4 (d, *J* = 12.0 Hz); 128.3 (d, *J* = 11.9 Hz); 127.6; 127.5; 126.5; 124.8; 120.8; 73.9; 64.9; 36.9 (d, *J* = 70.2 Hz); 15.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.02.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{25}H_{25}NO_2P$ (M+H) 402.1617, found 402.1604.

IR (film) cm^{-1}: 3053, 2973, 2893, 1436, 1183, 1116, 724, 693.



methyl 1-(2-diphenylphosphoryl)-1-ethoxyethyl)isoquinoline-3-carboxylate (15)

Ethyl vinyl ether (40 µL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using methyl isoquinoline-3-carboxylate (0.0187 g, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 65%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.17 (silica, 5/95, MeOH/DCM).

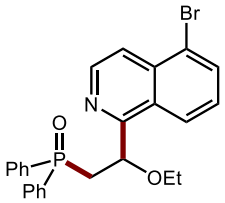
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71-8.66 (m, 1H); 8.38 (s, 1H); 7.92-7.89 (m, 1H); 7.88-7.83 (m, 2H); 7.75-7.70 (m, 2H); 7.61-7.56 (m, 2H); 7.53-7.49 (m, 1H); 7.48-7.44 (m, 2H); 7.32-7.28 (m, 1H); 7.24-7.19 (m, 2H); 5.79-5.73 (m, 1H); 4.02 (s, 3H); 3.39-3.29 (m, 2H); 3.27-3.17 (m, 2H); 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.4; 159.8 (d, *J* = 8.3 Hz); 140.5; 136.5; 133.8 (d, *J* = 100.6 Hz); 133.1 (d, *J* = 99.6 Hz); 131.7 (d, *J* = 2.2 Hz); 131.4 (d, *J* = 2.8 Hz); 131.2 (d, *J* = 9.6 Hz); 130.9 (d, *J* = 9.1 Hz); 130.8; 129.7; 128.9; 128.5 (d, *J* = 11.7 Hz); 128.2 (d, *J* = 11.9 Hz); 127.9; 125.5; 124.4; 75.9; 64.9; 52.8; 36.3 (d, *J* = 69.6 Hz); 15.2.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 28.81.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{27}H_{27}NO_4P$ (M+H) 460.1672, found 460.1660.

IR (film) cm^{-1}: 2922, 2851, 1719, 1670, 1559, 1437, 1296, 1245, 1208, 1178, 1117, 980, 909.



(2-(5-bromoisoquinolin-1-yl)-2-ethoxyethyl)diphenylphosphine oxide (16)

Ethyl vinyl ether (40 µL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using 5-bromoisoquinoline (0.0208 g, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 65%. Isolation by preparatory plate resulted in a clear oil.

R_f = 0.30 (silica, 5/95, MeOH/DCM).

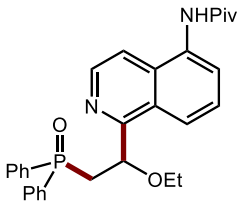
^{1}H NMR (850 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 5.8 Hz, 1H); 8.51 (d, *J* = 8.5 Hz, 1H); 7.94 (d, *J* = 7.4 Hz, 1H); 7.87-7.82 (m, 3H); 7.51-7.45 (m, 5H); 7.32-7.28 (m, 1H); 7.22-7.18 (m, 2H); 5.87-5.81 (m, 1H); 3.30-3.26 (m, 2H); 3.25-3.20 (m, 1H); 2.99-2.94 (m, 1H); 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (214 MHz, $CDCl_3$): δ = 159.9 (d, *J* = 9.3 Hz); 135.6; 133.9; 133.6 (d, *J* = 101.8 Hz); 133.0 (d, *J* = 98.9 Hz); 131.7 (d, *J* = 2.2 Hz); 131.4 (d, *J* = 2.1 Hz); 131.1 (d, *J* = 9.6 Hz); 130.5 (d, *J* = 9.4 Hz); 128.5 (d, *J* = 12.0 Hz); 128.3 (d, *J* = 11.6 Hz); 127.9 (s, overlap); 127.8 (s, overlap); 127.6; 124.6; 122.5; 119.8; 73.9; 65.0; 37.0 (d, *J* = 70.1 Hz); 15.1.

^{31}P NMR (163 MHz, $CDCl_3$): δ = 28.68.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{25}H_{24}BrNO_2P$ (M+H) 480.0723, found 480.0722.

IR (film) cm^{-1}: 3053, 2972, 2924, 1437, 1185, 1118, 1096.



N-(1-(2-(diphenylphosphoryl)-1-ethoxylethyl)isoquinolin-5-yl)pivalamide (17)

Ethyl vinyl ether (40 µL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using N-(isoquinolin-5-yl)pivalamide (0.0228 g, 0.1 mmol) instead of phenanthridine. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 69%. Isolation by preparatory plate resulted in a clear oil.

R_f = 0.20 (silica, 5/95, MeOH/DCM).

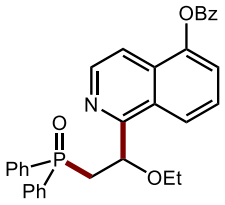
^{1}H NMR (850 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 5.9 Hz, 1H); 8.37 (d, *J* = 8.5 Hz, 1H); 8.09 (d, *J* = 7.5 Hz, 1H); 7.89-7.85 (m, 2H); 7.69 (s, broad, 1H); 7.63-7.57 (m, 3H); 7.53-7.44 (m, 1H); 7.49-7.45 (m, 2H); 7.43 (d, *J* = 5.2 Hz, 1H); 7.36-7.33 (m, 1H); 7.30-7.26 (m, 2H, overlap); 5.81 (td, *J* = 13.3, 4.4 Hz, 1H); 3.29-3.20 (m, 3H); 2.89 (ddd, *J* = 15.4, 12.8, 4.2 Hz, 1H); 1.44 (s, 9H); 0.84 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (214 MHz, $CDCl_3$): δ = 177.2; 160.3 (d, *J* = 10.7 Hz); 142.3; 133.53 (d, *J* = 98.8 Hz, overlap); 133.50 (d, *J* = 98.9 Hz, overlap); 132.5; 131.6 (d, *J* = 1.7 Hz); 131.5 (d, *J* = 2.0 Hz); 131.3 (d, *J* = 9.6 Hz); 131.1; 130.6 (d, *J* = 9.4 Hz); 128.5 (d, *J* = 11.9 Hz, overlap); 128.4 (d, *J* = 11.8 Hz, overlap); 127.6; 126.8; 125.2; 122.3; 113.8; 74.3, 65.0; 40.0; 36.9 (d, *J* = 69.8 Hz); 27.9; 15.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.06.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{30}H_{34}N_2O_3P$ (M+H) 501.2302, found 501.2301.

IR (film) cm^{-1}: 3236, 2966, 2925, 1670, 1521, 1484, 1177, 1118.



1-(2-(diphenylphosphoryl)-1-ethoxyethyl)isoquinolin-5-yl)benzoate (18)

Ethyl vinyl ether (40 μL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using isoquinolin-5-yl benzoate (0.0249 g, 0.1 mmol) instead of phenanthridine. Dichloroethane was used as an internal standard and ^{1}H NMR yield was determined to be 69%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.23 (silica, 5/95, MeOH/DCM).

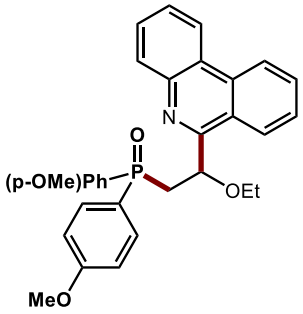
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.50-8.44 (m, 2H); 8.33-8.28 (m, 2H); 7.91-7.84 (m, 2H); 7.74-7.69 (m, 1H); 7.69-7.63 (m, 1H); 7.61-7.44 (m, 9H); 7.37-7.32 (m, 1H); 7.29-7.23 (m, 2H, overlap); 5.84 (ddd, *J* = 9.1, 8.4, 4.6 Hz, 1H); 3.34-3.19 (m, 3H); 2.96 (ddd, *J* = 15.1, 12.2, 4.7 Hz, 1H); 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.0; 159.8 (d, *J* = 9.3 Hz); 146.4; 142.6; 134.3; 133.6 (d, *J* = 101.0 Hz); 133.2 (d, *J* = 98.9 Hz); 131.9; 131.6 (d, *J* = 2.1 Hz); 131.5 (d, *J* = 2.2 Hz); 131.2 (d, *J* = 9.6 Hz); 130.6 (d, *J* = 9.5 Hz); 130.5; 129.0; 128.7 (d, *J* = 11.8 Hz); 128.5 (d, *J* = 12.1 Hz); 127.4; 127.2; 122.9; 122.5; 114.3; 74.4; 65.1; 37.0 (d, *J* = 70.1 Hz); 15.0.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 29.22.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{32}H_{29}NO_4P$ (M+H) 522.1829, found 522.1809.

IR (film) cm^{-1}: 3057, 2924, 2854, 2360, 1739, 1676, 1588, 1559, 1437, 1263, 1227, 1142, 1118, 1056, 1023, 998.



(2-ethoxy-2-(phenanthridine-6-yl)ethyl)bis(4-methoxyphenyl)phosphine oxide (19)

Ethyl vinyl ether (40 μL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using bis(4-methoxyphenyl)phosphine oxide (0.0524 g, 0.2 mmol) instead of diphenylphosphine oxide. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 80%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.25 (silica, 5/95, MeOH/DCM).

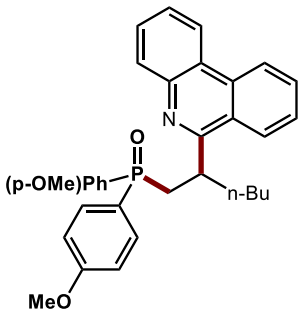
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 8.1 Hz, 1H); 8.58 (d, *J* = 8.2 Hz, 1H); 8.49 (dm, *J* = 8.1 Hz, 1H); 8.14 (dd, *J* = 8.1, 1.0 Hz, 1H); 7.84-7.80 (m, 1H); 7.75-7.68 (m, 4H); 7.65-7.62 (m, 1H); 7.37-7.31 (m, 2H); 6.95-6.92 (m, 2H); 6.49-6.45 (m, 2H); 5.83-5.78 (m, 1H); 3.83 (s, 3H); 3.62 (s, 3H); 3.42 (q, *J* = 7.0 Hz, 2H); 3.20-3.16 (m, 2H); 1.00 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.3 (d, *J* = 2.6 Hz); 161.7 (d, *J* = 1.7 Hz); 159.5 (d, *J* = 7.4 Hz); 143.4; 133.3; 132.9 (d, *J* = 11.0 Hz); 132.5 (d, *J* = 10.7 Hz); 130.5; 130.5; 128.5; 127.5; 127.1; 126.2; 125.4 (d, *J* = 106.9 Hz); 124.6; 124.2; 124.1 (d, *J* = 105.9 Hz); 122.4; 121.8; 114.0 (d, *J* = 13.1 Hz); 113.5 (d, *J* = 12.7 Hz); 75.6; 64.9; 55.4; 55.2; 37.0 (d, *J* = 70.7 Hz); 15.3.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 28.82.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{31}H_{31}NO_4P$ (M+H) 512.1985, found 512.1980.

IR (film) cm^{-1}: 2971, 2837, 1596, 1502, 1254, 1175, 1119, 729.



bis(4-methoxyphenyl)(2-(phenanthridine-6-yl)hexyl)phosphine oxide (20)

1-hexene (25 µL, 0.2 mmol) was subjected to **GP3** without DI H_2O, using bis(4-methoxyphenyl)phosphine oxide (0.0524 g, 0.2 mmol) instead of diphenylphosphine oxide, and using $Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ as a photocatalyst instead of $Ir(ppy)_2(dtbbpy)PF_6$. Dibromomethane was used as an internal standard and ^1H NMR yield was determined to be 65%. Isolation by preparatory plate resulted in a clear oil.

R_f = 0.40 (silica, 5/95, MeOH/DCM).

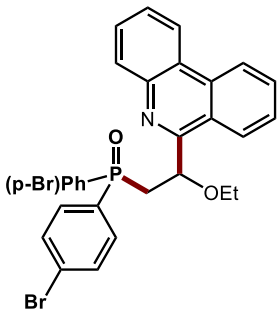
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 8.3 Hz, 1H); 8.41 (d, *J* = 8.1 Hz, 1H); 8.28 (d, *J* = 8.3 Hz, 1H); 7.99 (dd, *J* = 8.1, 1.0 Hz, 1H); 7.75-7.73 (m, 1H); 7.68-7.65 (m, 3H); 7.63-7.60 (m, 1H); 7.59-7.56 (m, 1H); 6.99 (dd, *J* = 11.3, 8.5 Hz, 2H); 6.91 (dd, *J* = 9.0, 2.0 Hz, 2H); 5.95 (dd, *J* = 9.0, 2.0 Hz, 2H); 4.44-4.39 (m, 1H); 3.80 (s, 3H); 3.52-3.47 (m, 1H); 3.41 (s, 3H); 2.70 (td, *J* = 23.2, 2.8 Hz, 1H); 2.11-2.05 (m, 1H); 1.90-1.84 (m, 1H); 1.30-1.19 (m, 3H); 1.11-1.04 (m, 1H); 0.75 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7 (d, *J* = 2.7 Hz); 162.2 (d, *J* = 2.6 Hz); 160.9 (d, *J* = 2.5 Hz); 143.6; 132.5 (s, overlap); 132.4 (d, *J* = 10.4 Hz, overlap); 132.4 (d, *J* = 10.5 Hz, overlap); 130.1; 129.7; 128.2; 127.2; 126.4 (d, *J* = 104.0 Hz, overlap); 126.2; 126.2; 125.8; 123.6; 122.7 (d, *J* = 103.5 Hz); 121.9; 121.7; 114.1 (d, *J* = 12.4 Hz); 112.6 (d, *J* = 12.5 Hz); 55.4; 54.9; 38.2 (d, *J* = 12.2 Hz); 36.1 (d, *J* = 71.6 Hz); 34.9; 29.6; 22.9; 14.0.

^{31}P NMR (162MHz, $CDCl_3$): δ = 30.38.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{33}H_{35}NO_3P$ (M+H) 524.2355, found 524.2348.

IR (film) cm^{-1}: 2955, 2928, 1596, 1502, 1254, 1119.



bis(4-bromophenyl)(2-ethoxy-2-(phenanthridine-6-yl)ethyl)phosphine oxide (21)

Ethyl vinyl ether (40 μL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using bis(4-bromophenyl)phosphine oxide (0.0720 g, 0.2 mmol) instead of diphenylphosphine oxide. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 72%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.20 (silica, 5/95, MeOH/DCM).

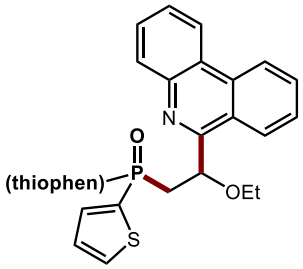
^{1}H NMR (850 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.2 Hz, 1H); 8.61 (d, *J* = 8.2 Hz, 1H); 8.52 (d, *J* = 8.0 Hz, 1H); 8.11 (dd, *J* = 8.1, 0.8 Hz, 1H); 7.86-7.83 (m, 1H); 7.74-7.69 (m, 2H); 7.68-7.64 (m, 3H); 7.60-7.58 (m, 2H); 7.25-7.20 (m, 2H); 7.09-7.06 (m, 2H); 5.85-5.81 (m, 1H); 3.47-3.42 (m, 2H); 3.26-3.18 (m, 2H); 1.01 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (213 MHz, $CDCl_3$): δ = 158.8 (d, *J* = 7.0 Hz); 143.2; 133.3, 132.5 (d, *J* = 101.7 Hz); 132.5 (d, *J* = 10.3 Hz); 132.3 (d, *J* = 107.5 Hz, overlap); 132.0 (d, *J* = 9.9 Hz, overlap); 131.9 (d, *J* = 12.6 Hz, overlap); 131.3 (d, *J* = 12.1 Hz); 130.7; 130.3; 128.8; 127.6; 127.5; 127.1 (d, *J* = 3.2 Hz); 126.6 (d, *J* = 3.5 Hz); 125.8; 124.5; 124.2; 122.6; 122.0; 75.3; 65.0, 36.4 (d, *J* = 70.9 Hz); 15.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.90.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{29}H_{25}Br_2NO_2P$ (M+H) 607.9984, found 607.9994.

IR (film) cm^{-1}: 3075, 2923, 2852, 2359, 1670, 1576, 1478, 1443, 1384, 1181, 1116, 1093, 1067, 1009, 907.



(2-ethoxy-2-(phenanthridine-6-yl)ethyl)di(thiophen-2-yl)phosphine oxide (22)

Ethyl vinyl ether (40 µL, 0.4 mmol) was subjected to **GP3** with 2 mL of DMSO and without TFA, using (dithiophen)phosphine oxide (0.0428 g, 0.2 mmol) instead of diphenylphosphine oxide. Dichloroethane was used as an internal standard and ^{1}H NMR yield was determined to be 80%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.23 (silica, 5/95, MeOH/DCM).

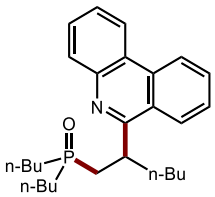
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.74 (dd, *J* = 8.4, 0.6 Hz, 1H); 8.63 (d, *J* = 8.3 Hz, 1H); 8.53 (dd, *J* = 8.0, 1.0 Hz, 1H); 8.15 (dd, *J* = 8.0, 1.2 Hz, 1H); 7.87-7.80 (m, 1H); 7.74-7.68 (m, 4H); 7.67-7.63 (m, 1H); 7.50-7.47 (m, 1H); 7.44 (ddd, *J* = 7.4, 3.6, 1.1 Hz, 1H); 7.19 (ddd, *J* = 4.7, 3.6, 1.9 Hz, 1H); 6.92 (ddd, *J* = 4.8, 3.6, 1.9 Hz, 1H); 5.81 (ddd, *J* = 10.8, 8.2, 4.9 Hz, 1H); 3.45 (q, *J* = 7.0 Hz, 2H); 3.32 (ddd, *J* = 15.2, 10.5, 8.2 Hz, 1H); 3.18 (ddd, *J* = 15.3, 13.1, 5.0 Hz, 1H); 1.01 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.0 (d, *J* = 10.3 Hz); 143.3; 135.8 (d, *J* = 10.4 Hz); 135.4 (d, *J* = 10.2 Hz, overlap); 134.8 (d, *J* = 115.6 Hz, overlap); 134.4 (d, *J* = 114.2 Hz, overlap); 133.5; 133.4 (d, *J* = 5.2 Hz); 133.2 (d, *J* = 5.1 Hz); 130.7; 130.5; 128.7; 128.2 (d, *J* = 14.4 Hz); 128.0 (d, *J* = 14.3 Hz); 127.6; 127.3; 126.2; 124.3; 124.2; 122.6; 121.9; 76.6 (d, *J* = 2.1 Hz); 65.0; 40.1 (d, *J* = 78.5 Hz); 15.2.

^{31}P NMR (243 MHz, $CDCl_3$): δ = 19.09.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{25}H_{23}NO_2PS_2$ (M+H) 464.0902, found 464.0888.

IR (film) cm^{-1}: 3069, 2973, 2923, 2225, 1611, 1573, 1526, 1501, 1486, 1405, 1334, 1219, 1182, 1116, 1093, 1016, 907.



dibutyl(2-(phenanthridin-6-yl)hexyl)phosphine oxide (23)

1-hexene (0.125 mL, 1.0 mmol) was subjected to **GP3** without DI H_2O, using dibutyl phosphine oxide (0.0324 g, 0.2 mmol) instead of diphenylphosphine oxide, and using Ir(dF-CF_3-ppy)$_2$(dtbbpy)PF_6 as a photocatalyst instead of Ir(ppy)$_2$(dtbbpy)PF_6. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 29%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.43 (alumina, 2/98, methanol/DCM).

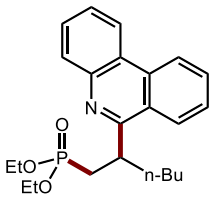
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 8.2 Hz, 1H); 8.56 (dd, *J* = 8.1, 1.3 Hz, 1H); 8.45 (d, *J* = 8.3 Hz, 1H); 8.09 (dd, *J* = 8.1, 1.0 Hz, 1H); 7.88-7.82 (m, 1H); 7.76-7.68 (m, 2H); 7.67-7.60 (m, 1H); 4.40-4.29 (m, 1H); 3.06 (ddd, *J* = 15.0, 9.9, 6.3 Hz, 1H); 2.15 (td, *J* = 22.9, 2.8 Hz, 1H); 2.07-1.96 (m, 1H); 1.87-1.78 (m, 1H); 1.60-1.48 (m, 4H); 1.37-1.27 (m, 4H, overlap with grease); 1.25-1.14 (m, 4H, overlap with grease); 1.13-1.06 (m, 1H); 1.04-0.89 (m, 2H); 0.85 (t, *J* = 7.3 Hz, 3H, overlap); 0.80 (t, *J* = 7.0 Hz, 3H, overlap); 0.76-0.67 (m, 1H); 0.48 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.2 (d, *J* = 2.3 Hz); 143.5; 133.1; 130.6; 129.8; 128.6; 127.8; 126.7; 125.9; 125.4; 123.7; 122.6; 122.1; 38.4 (d, *J* = 11.2 Hz); 35.5 (s, broad); 31.7 (d, *J* = 63.9 Hz); 29.6; 29.1 (d, *J* = 65.0 Hz); 28.4 (d, *J* = 63.7 Hz); 24.4 (d, *J* = 14.1 Hz); 24.1 (d, *J* = 15.1 Hz, overlap); 24.0 (d, *J* = 3.3 Hz, overlap); 23.6 (d, *J* = 4.0 Hz); 22.9; 14.05; 13.7; 13.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 48.71.

HRMS (ESI-TOF) m/z: calc'd for $C_{27}H_{38}NOP$ (M+H) 424.2764, found 424.2744.

IR (film) cm^{-1}: 2955, 2928, 2870, 2359, 2342, 1577, 1488, 1459, 1303, 1227, 1142, 1093, 907, 761, 726.



diethyl-(2-(phenanthridin-6-yl)hexyl)phosphonate (24)

1-hexene (25 µL, 0.2 mmol) was subjected to **GP3** without DI H_2O, using diethyl phosphonate (26 µL, 0.2 mmol) instead of diphenylphosphine oxide, and using $Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ as a photocatalyst instead of $Ir(ppy)_2(dtbbpy)PF_6$. Dibromomethane was used as an internal standard and ^1H NMR yield was determined to be 44%. Isolation by preparatory plate resulted in a clear oil.

R_f: 0.37 (silica, 5/95, methanol/DCM).

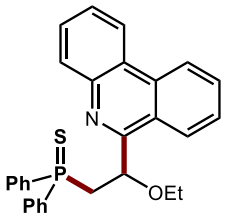
^1H NMR (600 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 8.2 Hz, 1H); 8.56 (d, *J* = 8.2 Hz, 1H); 8.40 (d, *J* = 8.2 Hz, 1H); 8.10 (dd, *J* = 8.1, 0.99 Hz, 1H); 7.85-7.82 (m, 1H); 7.73-7.69 (m, 2H); 7.64-7.61 (m, 1H); 4.26-4.20 (m, 1H); 3.91-3.85 (m, 1H); 3.82-3.76 (m, 3H); 3.00-2.94 (m, 1H); 2.29-2.23 (m, 1H); 2.08-2.02 (m, 1H); 1.88-1.83 (m, 1H); 1.30-1.23 (m, 3H, grease overlap); 1.19-1.14 (m, 1H); 0.97-0.92 (m, 6H); 0.79 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.36 (d, *J* = 5.6 Hz); 143.73; 133.02; 130.32; 129.93; 128.57; 127.47; 126.49; 125.81; 125.64; 123.52; 122.57; 122.01; 61.38 (d, *J* = 6.1 Hz); 61.18 (d, *J* = 6.5 Hz); 37.08 (d, *J* = 13.7 Hz); 36.17 (s, broad); 30.07 (d, *J* = 138.3 Hz); 29.57; 22.88; 16.16 (d, *J* = 6.6 Hz, overlap); 16.11 (d, *J* = 6.7 Hz); 14.06.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.48.

HRMS (ESI-TOF) m/z: calc'd for $C_{23}H_{31}NO_3P$ (M+H) 400.2036, found 400.2031.

IR (film) cm^{-1}: 2955, 2925, 1238, 1054, 1026, 962.



(2-ethoxy-2-(phenanthridine-6-yl)ethyl)diphenyl phosphine sulfide (25)

Ethyl vinyl ether (19 μL, 0.2 mmol) was subjected to **GP3**, using diphenylphosphine sulfide (0.0437 g, 0.2 mmol) instead of diphenylphosphine oxide. Dichloroethane was used as an internal standard and ^{1}H NMR yield was determined to be 79%. Isolation by preparatory plate resulted in a light yellow oil.

R_f = 0.33 (silica, 100% DCM).

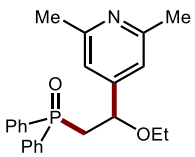
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 8.0 Hz, 1H); 8.60 (d, *J* = 8.3 Hz, 1H); 8.50 (dd, *J* = 8.1, 1.4 Hz, 1H); 8.17 (dd, *J* = 8.0, 1.1 Hz, 1H); 8.04-7.97 (m, 2H); 7.86-7.80 (m, 1H); 7.74-7.67 (m, 2H); 7.67-7.59 (m, 3H); 7.52-7.44 (m, 3H); 7.20-7.15 (m, 1H); 7.13-7.07 (m, 2H); 6.16-6.08 (m, 1H); 3.53-3.39 (m, 3H); 3.21 (ddd, *J* = 14.5, 11.8, 4.4 Hz, 1H); 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3 (d, *J* = 10.8 Hz); 143.4; 133.4 (d, *J* = 81.7 Hz); 133.3; 133.0 (d, *J* = 81.6 Hz); 131.7 (d, *J* = 10.5 Hz); 131.3 (d, *J* = 3.0 Hz); 131.0 (d, *J* = 10.0 Hz, overlap); 130.9 (d, *J* = 2.9 Hz, overlap); 130.6; 130.4; 128.6; 128.4 (d, *J* = 12.5 Hz); 128.1 (d, *J* = 12.0 Hz); 127.6; 127.1; 126.1; 124.5; 124.1; 122.4; 121.9; 75.5; 65.1; 38.6 (d, *J* = 55.0 Hz); 15.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.65.

HRMS (ESI-TOF) *m/z*: calc'd for $C_{29}H_{27}NOPS$ (M+H) 468.1545, found 468.1544.

IR (film) cm^{-1}: 3055, 2972, 2923, 2360, 1611, 1574, 1526, 1482, 1459, 1436, 1103, 909.



(2-(2,6-dimethylpyridin-4-yl)-2-ethoxyethyl)diphenylphosphine oxide (26)

1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate (0.0249 g, 0.1 mmol) was subjected to **GP4**. Isopropyl acetate was used as an internal standard and ^{1}H NMR yield was determined to be 81%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.67 (alumina, 5/95, methanol/DCM).

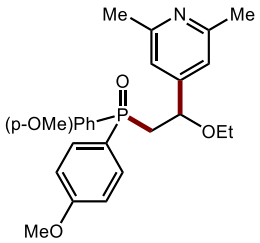
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.76 (m, 2H); 7.67-7.58 (m, 2H); 7.54-7.41 (m, 4H); 7.41-7.32 (m, 2H); 6.87 (s, 2H); 4.78 (td, *J* = 13.2, 4.3 Hz, 1H); 3.28-3.12 (m, 2H); 2.93-2.81 (m, 1H); 2.54-2.45 (m, 1H, overlap); 2.44 (s, 6H); 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2; 151.8 (d, *J* = 9.5 Hz); 133.6 (d, *J* = 99.7 Hz); 133.5 (d, *J* = 101.2 Hz); 131.7 (d, *J* = 2.5 Hz); 131.6 (d, *J* = 2.8 Hz); 131.1 (d, *J* = 9.8 Hz); 130.6 (d, *J* = 9.3 Hz); 128.5 (d, *J* = 11.4 Hz, overlap); 128.4 (d, *J* = 10.6 Hz, overlap); 117.9; 75.0 (d, *J* = 2.9 Hz); 64.9; 39.2 (d, *J* = 69.7 Hz); 24.5; 14.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.26.

HRMS (ESI-TOF) m/z: calc'd for $C_{23}H_{27}NO_2P$ (M+H) 380.1774, found 380.1764.

IR (film) cm^{-1}: 3055, 2974, 2925, 2360, 2342, 2219, 1606, 1570, 1437, 1400, 1381, 1335, 1179, 1117, 1094, 729, 717, 694.



(2-(2,6-dimethylpyridin-4-yl)-2-ethoxyethyl)bis(4-methoxyphenyl)phosphine oxide (27)

1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate (0.0249 g, 0.1 mmol) was subjected to **GP4** without DI H2O, without sodium carbonate, substituting bis(4-methoxyphenyl)phosphine oxide (0.0524 g, 0.2 mmol) instead of diphenylphosphine oxide, and substituting $Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ as a photocatalyst instead of $Ir(ppy)_2(dtbbpy)PF_6$. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 57%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.31 (silica, 5/95, methanol/DCM).

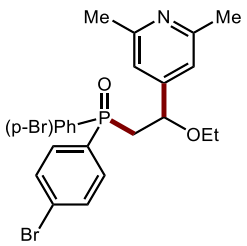
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.68 (m, 2H); 7.55-7.50 (m, 2H); 6.98-6.95 (m, 2H); 6.88-6.85 (m, 2H, overlap); 6.86 (s, 2H, overlap); 4.73 (td, *J* = 13.2, 4.4 Hz, 1H); 3.84 (s, 3H); 3.80 (s, 3H); 3.26-3.20 (m, 1H); 3.20-3.15 (m, 1H); 2.84-2.77 (m, 1H); 2.45 (s, 6H, overlap); 2.45-2.39 (m, 1H, overlap); 0.91 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (d, *J* = 2.1 Hz, overlap); 162.2 (d, *J* = 2.2 Hz, overlap); 158.14; quaternary carbon at approx. 153 not observed; 133.0 (d, *J* = 11.0 Hz); 132.3 (d, *J* = 10.7 Hz); 125.0 (d, *J* = 106.5 Hz, overlap); 125.0 (d, *J* = 105.2 Hz, overlap); 118.0; 114.0 (d, *J* = 12.0 Hz, overlap); 113.9 (d, *J* = 13.9 Hz, overlap); 75.2 (d, *J* = 2.0 Hz); 64.9; 55.4 (s, overlap); 55.4 (s, overlap); 39.6 (d, *J* = 70.6 Hz); 24.5; 15.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.52.

HRMS (ESI-TOF) m/z: calc'd for $C_{25}H_{31}NO_4P$ (M+H) 440.1985, found 440.1976.

IR (film) cm^{-1}: 3385, 2972, 2840, 2361, 1595, 1569, 1502, 1458, 1441, 1405, 1292, 1252, 1165, 1117, 1100, 1023, 827, 864, 802.



Bis(4-bromophenyl)(2-(2,6-dimethylpyridin-4-yl)2-ethoxyethyl)phosphine oxide (28)

1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate (0.0249 g, 0.1 mmol) was subjected to **GP4**, substituting bis(4-bromophenyl)phosphine oxide instead of diphenylphosphine oxide, and substituting $Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ as a photocatalyst instead of $Ir(ppy)_2(dtbbpy)PF_6$. Dibromomethane was used as an internal standard and ^1H NMR yield was determined to be 50%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.17 (silica, 5/95, methanol/DCM).

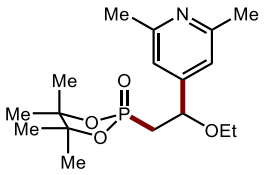
^1H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.60 (m, 4H); 7.55-7.51 (m, 2H); 7.50-7.44 (m, 2H); 6.86 (s, 2H); 4.76 (td, *J* = 13.6, 3.7 Hz, 1H); 3.28-3.12 (m, 2H); 2.78 (ddd, *J* = 15.2, 9.3, 6.8 Hz, 1H); 2.47 (s, 6H, overlap); 2.45-2.39 (m, 1H, overlap); 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4; 151.5 (d, *J* = 10.1 Hz); 132.6 (d, *J* = 10.5 Hz, overlap); 132.4 (d, *J* = 98.8 Hz, overlap); 132.2 (d, *J* = 100.6 Hz, overlap); 132.0 (d, *J* = 11.2 Hz, overlap); 131.8 (d, *J* = 12.5 Hz); 127.2 (d, *J* = 3.1 Hz); 127.0 (d, *J* = 3.3 Hz); 117.8; 74.9 (d, *J* = 3.1 Hz); 65.0; 39.0 (d, *J* = 71.0 Hz); 24.5; 14.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.77.

HRMS (ESI-TOF) m/z: calc'd for $C_{23}H_{25}Br_2NO_2P$ (M+H) 535.9984, found 535.9961.

IR (film) cm^{-1}: 2973, 2359, 1605, 1575, 1479, 1384, 1336, 1181, 1114, 1094, 1067, 1009.



2-(2-(2,6-dimethylpyridin-4-yl)-2-ethoxyethyl)-4,4,5,5-tetramethyl-1,3,2-dioxophospholane 2-oxide (29)

1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate (0.0249 g, 0.1 mmol) was subjected to **GP4** without DI H2O, without sodium carbonate, substituting 4,4,5,5-tetramethyl-1,3,2-dioxophospholane 2-oxide instead of diphenylphosphine oxide, and substituting $Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ as a photocatalyst instead of $Ir(ppy)_2(dtbbpy)PF_6$. Dibromomethane was used as an internal standard and ^1H NMR yield was determined to be 50%. Isolation by preparatory plate resulted in a clear oil.

R_f: 0.32 (silica, 5/95, methanol/DCM).

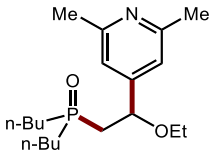
^1H NMR (400 MHz, $CDCl_3$): δ = 6.96 (s, 2H); 4.68 (td, *J* = 13.3, 5.0 Hz, 1H); 3.54-3.39 (m, 2H); 2.52 (s, 6H); 2.33-2.21 (m, 2H); 1.50 (s, 3H); 1.44 (s, 3H); 1.35 (s, 3H); 1.25 (s, 3H); 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3; 151.7 (d, *J* = 13.7 Hz); 117.9; 88.0 (d, *J* = 80.1 Hz); 76.0 (d, *J* = 3.4 Hz); 65.5; 38.1 (d, *J* = 132.0 Hz); 24.9 (d, *J* = 3.4 Hz); 24.6 (d, *J* = 3.4 Hz, overlap); 24.6 (s, overlap); 24.1 (d, *J* = 4.8 Hz); 24.0 (d, *J* = 5.7 Hz); 15.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.96.

HRMS (ESI-TOF) m/z: calc'd for $C_{17}H_{29}NO_4P$ (M+H) 342.1829, found 342.1815.

IR (film) cm^{-1}: 2981, 2927, 1607, 1571, 962, 932.



Dibutyl(2-(2,6-dimethylpyridin-4-yl)-2-ethoxyethyl)phosphine oxide (30)

1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate (0.0249 g, 0.1 mmol) was subjected to **GP4**, substituting dibutylphosphine oxide instead of diphenylphosphine oxide, and substituting Ir(dF-CF_3-ppy)$_2$(dtbbpy)PF_6 as a photocatalyst instead of Ir(ppy)$_2$(dtbbpy)PF_6. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 37%. Isolation by preparatory plate resulted in a low-melting white solid.

R_f: 0.47 (alumina, 5/95, methanol/DCM).

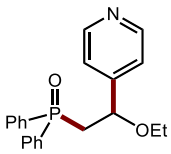
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (s, 2H); 4.73-4.65 (m, 1H); 3.44-3.30 (m, 2H); 2.51 (s, 6H); 2.10-2.02 (m, 1H, overlap); 1.98-1.80 (m, 3H, overlap); 1.61-1.32 (m, 10H, overlap); 1.17 (t, *J* = 7.0 Hz, 3H); 0.95 (t, *J* = 7.2 Hz, 3H); 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4; 152.4 (d, *J* = 10.9 Hz); 117.7; 75.3 (d, *J* = 4.0 Hz); 64.9; 36.9 (d, *J* = 61.9 Hz); 29.0 (d, *J* = 65.6 Hz); 28.9 (d, *J* = 65.6 Hz); 24.6; 24.4 (d, *J* = 12.9 Hz); 24.3 (d, *J* = 11.8 Hz); 24.1 (d, *J* = 3.6 Hz); 23.7 (d, *J* = 3.8 Hz); 15.3; 13.7; 13.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 46.71.

HRMS (ESI-TOF) m/z: calc'd for $C_{19}H_{35}NO_2P$ (M+H) 340.2400, found 340.2395.

IR (film) cm^{-1}: 2957, 2929, 2871, 2359, 2341, 1606, 1570, 1400, 1380, 1339, 1223, 1147, 1114, 1093, 904, 818, 668.



(2-ethoxy-2-(pyridine-4-yl)ethyl)diphenylphosphine oxide (31)

1-methoxypyridin-1-ium methyl sulfate (0.0221 g, 0.1 mmol) was subjected to **GP4**. Dichloroethane was used as an internal standard and ^{1}H NMR yield was determined to be 54% (for substitution at the 4 position) and 18% (for substitution at the 2 position) (72% total). Isolation by preparatory plate resulted in a light yellow oil (only for major isomer).

R_f: 0.43 (alumina, 5/95, methanol/DCM).

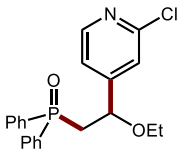
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (dd, *J* = 4.4, 1.4 Hz, 2H); 7.85-7.78 (m, 2H); 7.67-7.60 (m, 2H); 7.53-7.42 (m, 4H); 7.40-7.34 (m, 2H); 7.23 (dd, *J* = 4.5, 1.4 Hz, 2H); 4.86 (td, *J* = 13.6, 3.9 Hz, 1H); 3.26-3.13 (m, 2H); 2.86 (ddd, *J* = 15.1, 7.1, 9.1 Hz, 1H); 2.49 (ddd, *J* = 15.1, 13.1. 3.9 Hz, 1H); 0.83 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4 (d, *J* = 10.1 Hz); 150.2; 133.6 (d, *J* = 99.8 Hz); 133.4 (d, *J* = 101.42 Hz); 131.8 (d, *J* = 2.7 Hz); 131.6 (d, *J* = 2.7 Hz); 131.1 (d, *J* = 9.8 Hz); 130.5 (d, *J* = 9.5 Hz); 128.6 (d, *J* = 11.8 Hz); 128.4 (d, *J* = 12.3 Hz); 121.3; 74.9 (d, *J* = 3.0 Hz); 65.0; 39.3 (d, *J* = 70.1 Hz); 14.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.30.

HRMS (ESI-TOF) m/z: calc'd for $C_{21}H_{23}NO_2P$ (M+H) 352.1461, found 352.1459.

IR (film) cm^{-1}: 3055, 2974, 2877, 2358, 1599, 1563, 1483, 1437, 1414, 1311, 1169, 1116, 1096, 996, 824, 735, 715, 693, 566, 534, 506.



(2-(2-chloropyridin-4-yl)-2-ethoxyethyl)diphenylphosphine oxide (32a)

2-chloro-1-methoxypyridin-1-ium methyl sulfate (0.0256 g, 0.1 mmol) was subjected to **GP4**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 39%. Isolation by preparatory plate resulted in light yellow oil.

R_f: 0.20 (alumina, 1/99, methanol/DCM).

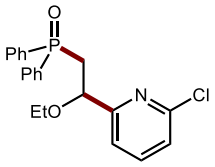
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 5.0 Hz, 1H); 7.84-7.77 (m, 2H); 7.67-7.59 (m, 2H); 7.55-7.44 (m, 4H); 7.42-7.36 (m, 2H); 7.27 (s, 1H); 7.16 (dd, *J* = 5.1, 1.3 Hz, 1H); 4.87 (td, *J* = 12.9, 4.3 Hz, 1H); 3.29-3.16 (m, 2H); 2.92-2.82 (m, 1H); 2.48 (ddd, *J* = 15.1, 12.6, 4.1 Hz, 1H); 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0 (d, *J* = 9.5 Hz); 152.1; 150.0; 133.3 (d, *J* = 100.0 Hz); 133.2 (d, *J* = 102.0 Hz); 131.9 (d, *J* = 2.5 Hz); 131.8 (d, *J* = 2.5 Hz); 131.0 (d, *J* = 9.7 Hz); 130.5 (d, *J* = 9.3 Hz); 128.7 (d, *J* = 11.8 Hz); 128.5 (d, *J* = 11.9 Hz); 121.9; 120.2; 74.6 (d, *J* = 2.3 Hz); 65.3; 39.1 (d, *J* = 69.8 Hz); 14.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.98.

HRMS (ESI-TOF) m/z: calc'd for $C_{21}H_{21}ClNO_2PNa$ (M+Na) 408.0891, found 408.0884.

IR (film) cm^{-1}: 3421, 3055, 2974, 2925, 2360, 2343, 1591, 1550, 1437, 1382, 1180, 1119, 1096, 997, 750, 695.



(2-(6-chloropyridin-2-yl)-2-ethoxyethyl)diphenylphosphine oxide (32b)

2-chloro-1-methoxypyridin-1-ium methyl sulfate (0.0256 g, 0.1 mmol) was subjected to **GP4**. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 16%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.20 (alumina, 1/99, methanol/DCM)

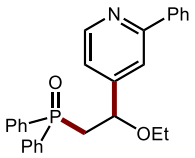
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.77 (m, 2H); 7.72-7.66 (m, 2H); 7.54 (t, *J* = 7.7 Hz, 1H); 7.50-7.36 (m, 6H); 7.28 (d, *J* = 7.5 Hz, 1H); 7.13 (dd, *J* = 7.9, 0.5 Hz, 1H); 4.92-4.89 (m, 1H); 3.34-3.25 (m, 2H); 2.89 (dd, *J* = 10.4, 6.6 Hz, 2H); 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (d, *J* = 10.1 Hz); 151.4; 139.2; 133.7 (d, *J* = 101.1 Hz); 133.5 (d, *J* = 99.4 Hz); 131.6 (d, *J* = 2.5 Hz, overlap); 131.5 (d, *J* = 2.8 Hz, overlap); 131.1 (d, *J* = 9.6 Hz); 130.8 (d, *J* = 9.4 Hz); 128.5 (d, *J* = 11.7 Hz, overlap); 128.4 (d, *J* = 11.9 Hz, overlap); 123.4; 119.8; 76.7 (d, *J* = 2.8 Hz); 65.3; 37.1 (d, *J* = 70.7 Hz); 14.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.65.

HRMS (ESI-TOF) m/z: calc'd for $C_{21}H_{21}ClNO_2PNa$ 408.0891, found 408.0873.

IR (film) cm^{-1}: 3413, 3056, 2973, 2924, 2632, 2344, 1581, 1560, 1436, 1178, 1118, 1101, 988, 719, 695.



(2-ethoxy-2-(2-phenylpyridin-4-yl)ethyl)diphenylphosphine oxide (33)

1-methoxy-2-phenylpyridin-1-ium methyl sulfate (0.0297 g, 0.1 mmol) was subjected to **GP4** without water and without base. Dichloroethane was used as an internal standard and ^{1}H NMR yield was determined to be 83% (major isomer, addition into the 4 position) and 13% (minor isomer, addition into the 2 position). Isolation by preparatory plate resulted in a light yellow oil (major isomer was isolated, minor was not).

R_f: 0.30 (silica, 5/95, methanol/DCM).

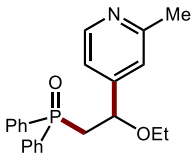
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (dd, *J* = 5.0, 0.6 Hz, 1H); 7.96-7.92 (m, 2H); 7.87-7.80 (m, 2H); 7.67-7.60 (m, 2H, overlap); 7.66 (s, 1H, overlap); 7.55-7.44 (m, 5H); 7.43-7.38 (m, 2H); 7.36-7.31 (m, 2H); 7.18 (dd, *J* = 5.0, 1.4 Hz, 1H); 4.95 (td, *J* = 13.2, 4.3 Hz, 1H); 3.33-3.19 (m, 2H); 2.93 (ddd, *J* = 15.1, 8.8, 7.6 Hz, 1H); 2.57 (ddd, *J* = 15.1, 12.7, 4.3 Hz, 1H); 0.88 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9; 152.2 (d, *J* = 9.7 Hz); 150.1; 139.2; 133.4 (d, *J* = 99.7 Hz); 133.4 (d, *J* = 101.4 Hz); 131.8 (d, *J* = 2.8 Hz); 131.6 (d, *J* = 2.7 Hz); 131.1 (d, *J* = 9.6 Hz); 130.5 (d, *J* = 9.5 Hz); 129.1; 128.8; 128.6 (d, *J* = 11.8 Hz); 128.4 (d, *J* = 12.0 Hz); 127.0; 119.7; 118.3; 75.2 (d, *J* =2.7 Hz); 65.0; 39.3 (d, *J* = 70.1 Hz); 14.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.24.

HRMS (ESI-TOF) m/z: calc'd for $C_{27}H_{27}NO_2P$ (M+H) 428.1774, found 428.1770.

IR (film) cm^{-1}: 3055, 2973, 2874, 2360, 1597, 1558, 1474, 1437, 1396, 1179, 1117, 1093.



(2-ethoxy-2-(2-methylpyridin-4-yl)ethyl)diphenylphosphine oxide (34)

1-methoxy-2-methylpyridin-1-ium methyl sulfate (0.0235 g, 0.1 mmol) was subjected to **GP4**. Isopropyl acetate was used as an internal standard and ^{1}H NMR yield was determined to be 70%. Isolation by preparatory plate resulted in a light yellow oil. Note, only single isomer observed.

R_f: 0.67 (alumina, 5/95, methanol/DCM).

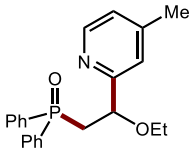
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (dd, *J* = 5.1, 0.4 Hz, 1H); 7.85-7.77 (m, 2H); 7.67-7.59 (m, 2H); 7.53-7.41 (m, 4H); 7.40-7.34 (m, 2H); 7.06 (s, 1H); 7.04 (dd, *J* = 5.2, 1.7 Hz, 1H); 4.82 (td, *J* = 13.4, 4.2 Hz, 1H); 3.27-3.12 (m, 2H); 2.86 (ddd, *J* = 15.1, 8.9, 7.5 Hz, 1H); 2.48 (ddd, *J* = 15.1, 12.8, 4.2 Hz, 1H, overlap); 2.47 (s, 3H, overlap); 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8; 151.6 (d, *J* = 9.7 Hz); 149.5; 133.6 (d, *J* = 99.8 Hz); 133.4 (d, *J* = 101.4 Hz); 131.7 (d, *J* = 2.8 Hz); 131.6 (d, *J* = 2.6 Hz); 131.1 (d, *J* = 9.7 Hz); 130.5 (d, *J* = 9.4 Hz); 128.6 (d, *J* = 11.8 Hz); 128.4 (d, *J* = 12.2 Hz); 120.9; 118.3; 75.0 (d, *J* = 2.9 Hz); 64.9; 39.2 (d, *J* = 70.1 Hz); 24.5; 14.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.27.

HRMS (ESI-TOF) m/z: calc'd for $C_{22}H_{25}NO_2P$ (M+H) 366.1617, found 366.1604.

IR (film) cm^{-1}: 3055, 2973, 2874, 2360, 2342, 1603, 1563, 1437, 1396, 1335, 1178, 1117, 1094, 998, 847, 749, 734, 715, 695.



(2-ethoxy-2-(4-methylpyridin-2-yl)ethyl)diphenylphosphine oxide (35)

1-methoxy-4-methylpyridin-1-ium methyl sulfate (0.0235 g, 0.1 mmol) was subjected to **GP4**. Isopropyl acetate was used as an internal standard and ^{1}H NMR yield was determined to be 52%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.60 (alumina, 5/95, methanol/DCM).

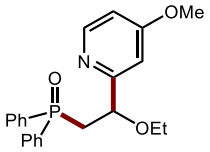
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 5.0 Hz, 1H); 7.86-7.77 (m, 2H); 7.70-7.62 (m, 2H); 7.50-7.37 (m, 4H); 7.37-7.31 (m, 2H); 7.09 (s, 1H); 6.90 (dd, *J* = 5.0, 0.8 Hz, 1H); 4.85 (td, *J* = 13.2, 4.4 Hz, 1H); 3.32-3.18 (m, 2H); 3.00-2.90 (m, 1H); 2.81 (ddd, *J* = 15.1, 12.3, 4.5 Hz, 1H); 2.26 (s, 3H); 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5 (d, *J* = 10.0 Hz); 149.5; 147.8; 133.8 (d, *J* = 100.1 Hz); 133.8 (d, *J* = 99.1 Hz); 131.4 (d, *J* = 2.9 Hz, overlap); 131.4 (d, *J* = 3.3 Hz, overlap); 131.1 (d, *J* = 9.6 Hz); 130.8 (d, *J* = 9.4 Hz); 128.4 (d, *J* = 11.7 Hz); 128.3 (d, *J* = 11.6 Hz); 123.7; 122.4; 76.9 (d, *J* = 2.7 Hz); 64.9; 37.4 (d, *J* = 70.8 Hz); 21.1; 14.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.11.

HRMS (ESI-TOF) m/z: calc'd for $C_{22}H_{25}NO_2P$ (M+H) 366.1617, found 366.1609.

IR (film) cm^{-1}: 3055, 2973, 2872, 2361, 1604, 1437, 1177, 1117, 1092, 996, 736, 715, 694.



(2-ethoxy-2-(4-methoxypyridin-2-yl)ethyl)diphenylphosphine oxide (36)

1,4-dimethoxypyridin-1-ium methyl sulfate (0.0251 g, 0.1 mmol) was subjected to **GP4**. Note, reaction does not proceed without a base. Dibromomethane was used as an internal standard and ^{1}H NMR yield was determined to be 36%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.56 (alumina, 5/95, methanol/DCM).

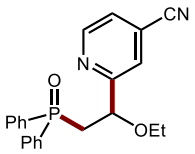
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 5.7 Hz); 7.86-7.79 (m, 2H); 7.73-7.67 (m, 2H); 7.52-7.40 (m, 4H); 7.40-7.34 (m, 2H); 6.85 (d, *J* = 2.5 Hz, 1H); 6.62 (dd, *J* = 5.7, 2.5 Hz, 1H); 4.84 (td, *J* = 13.5, 4.2 Hz, 1H); 3.80 (s, 3H); 3.35-3.19 (m, 2H); 2.93 (ddd, *J* = 15.2, 8.8, 8.5 Hz, 1H); 2.82 (ddd, *J* = 15.2, 12.3, 4.2 Hz, 1H); 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4; 162.8 (d, *J* = 10.3 Hz); 151.0; 133.8 (d, *J* = 100.2 Hz); 131.5 (d, *J* = 2.6 Hz); 131.2 (d, *J* = 9.6 Hz); 130.8 (d, *J* = 9.4 Hz); 128.5 (d, *J* = 10.9 Hz); 128.4 (d, *J* = 11.2 Hz); 109.0; 107.2; expected peak at ~77 likely hidden under calibrant peaks, but not observed; 65.1; 55.2; 37.5 (d, *J* = 70.7 Hz); 14.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.13.

HRMS (ESI-TOF) m/z: calc'd for $C_{22}H_{25}NO_3P$ (M+H) 382.1567, found 382.1556.

IR (film) cm^{-1}: 3405, 3056, 2973, 2926, 2360, 2342, 1597, 1568, 1482, 1437, 1303, 1177, 1119, 1099, 1034, 997, 736, 716, 696.



2-(2-(diphenylphosphoryl)-1-ethoxyethyl)isonicotinonitrile (37)

4-cyano-1-methoxypyridin-1-ium methyl sulfate (0.0251 g, 0.1 mmol) was subjected to **GP4**. Mesitylene was used as an internal standard and ^{1}H NMR yield was determined to be 57%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.67 (alumina, 5/95, methanol/DCM).

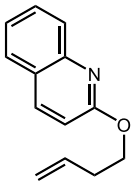
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (dd, *J* = 5.0, 0.8 Hz, 1H); 7.84-7.77 (m, 2H); 7.70-7.63 (m, 2H); 7.56 (t, *J* = 1.0 Hz, 1H); 7.53-7.42 (m, 4H); 7.41-7.36 (m, 2H); 7.33 (dd, *J* = 5.0, 1.5 Hz, 1H); 5.01 (ddd, *J* = 9.3, 7.1, 6.0 Hz, 1H); 3.39-3.29 (m, 2H); 2.92-2.83 (m, 2H); 0.92 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3 (d, *J* = 9.6 Hz); 150.6; 133.6 (d, *J* = 99.9 Hz); 133.4 (d, *J* = 101.3 Hz); 131.7 (d, *J* = 2.6 Hz); 131.1 (d, *J* = 9.6 Hz); 130.7 (d, *J* = 9.4 Hz); 128.6 (d, *J* = 11.2 Hz); 128.5 (d, *J* = 11.5 Hz); 124.1; 122.7; 121.0; 116.5; expected peak at ~77 likely hidden under calibrant peaks, but not observed; 65.7; 37.3 (d, *J* = 70.6 Hz); 14.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.15.

HRMS (ESI-TOF) m/z: calc'd for $C_{22}H_{22}N_2O_2P$ (M+H) 377.1413, found 377.1400.

IR (film) cm^{-1}: 3409, 3056, 2974, 2925, 2359, 2342, 2237, 1593, 1550, 1437, 1399, 1334, 1178, 1117, 997, 733, 715, 694.



2-(but-3-en-1-yloxy)quinoline (38)

A slightly modified literature procedure[8] was used to synthesize this compound. 2-chloroquinoline (0.33 g, 2.0 mmol) was added to a 20-mL vial equipped with a magnetic stir bar, followed by 3-buten-1-ol (3.44 mL, 40 mmol). The vial was evacuated 3x, and the atmosphere was replaced with N_2. Next, a KOtBu/tBuOH solution (1.0 M, 3.50 mL, 3.5 mmol) was added, and the vial was placed in a heating block set to 80°C for 24 hours. The reaction was quenched with 4 mL of saturated $NaHCO_3$ solution, then extracted with DCM (15 mL, 3x). The organic phase was collected, dried with Na_2SO_4, filtered, and condensed followed by a quick column (silica gel, ethyl acetate/hexanes gradient) in order to purify. The appropriate fractions were collected, condensed, and dried over high vacuum overnight to yield target compound (0.39 g, 98%) as a colorless oil.

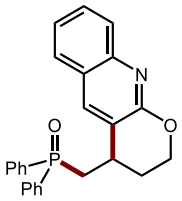
R_f: 0.50 (silica, 5/95, ethyl acetate/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.7 Hz, 1H); 7.83 (d, *J* = 8.3 Hz, 1H); 7.71 (dd, *J* = 8.0, 1.4 Hz, 1H); 7.64-7.58 (m, 1H); 7.39-7.34 (m, 1H); 6.90 (d, *J* = 8.8 Hz, 1H); 6.02-5.89 (m, 1H); 5.19 (dq, *J* = 17.2, 1.7 Hz, 1H); 5.13-5.09 (m, 1H); 4.54 (t, *J* = 6.8 Hz, 2H); 2.59 (qt, *J* = 11.3, 1.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 146.7, 138.7, 135.0, 129.5, 127.5, 127.3, 125.2, 124.0, 116.9, 113.3, 65.1, 33.5.

HRMS (ESI-TOF) m/z: calc'd for $C_{13}H_{14}NO$ (M+H) 200.1070, found 200.1063.

IR (film) cm^{-1}: 3065, 2948, 1617, 1605, 1572, 1427, 1312, 1276, 1257, 1240.



((3,4-dihydro-2H-pyrano[2,3-b]quinolin-4-yl)methyl)diphenylphosphine oxide (39)

2-(but-3-en-1-yloxy)quinoline (0.0199 g, 0.1 mmol) was subjected to **GP3**, without an alkene. Isopropyl acetate was used as an internal standard and ^{1}H NMR yield was determined to be 40%. Isolation by preparatory plate resulted in a light yellow oil.

R_f: 0.33 (silica, 50/50, acetonitrile/DCM).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.82-7.72 (m, 6H); 7.56-7.49 (m, 3H); 7.49-7.42 (m, 5H); 7.28 (t, *J* = 7.4 Hz, 1H); 4.47-4.41 (m, 1H); 4.39-4.34 (m, 1H); 3.65-3.58 (m, 1H); 2.81-2.74 (m, 1H); 2.65-2.57 (m, 1H); 2.27-2.20 (m, 1H); 2.07-2.01 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.2; 146.5; 137.7; 133.7 (d, *J* = 99.0 Hz); 132.7 (d, *J* = 99.0 Hz); 132.1 (d, *J* = 2.2 Hz); 132.0 (d, *J* = 3.3 Hz); 130.8 (d, *J* = 8.8 Hz); 130.6 (d, *J* = 8.8 Hz); 129.6; 129.0 (d, *J* = 11.0 Hz); 127.3; 127.0; 125.3; 124.2; 122.5 (d, *J* = 11.0 Hz); 64.5; 36.2 (d, *J* = 69.3 Hz); 29.6 (d, *J* = 3.3 Hz); 28.2 (d, *J* = 4.4 Hz).

^{31}P NMR (243 MHz, $CDCl_3$): δ = 29.61.

HRMS (ESI-TOF) m/z: calc'd for $C_{25}H_{23}NO_2P$ (M+H) 400.1461, found 400.1445.

IR (film) cm^{-1}: 3056, 2924, 2853, 2361, 2344, 1493, 1429, 1272, 1182, 1121.

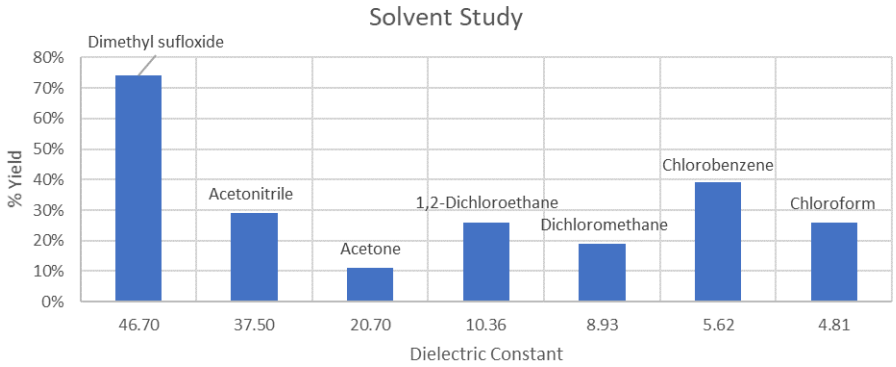
V. Mechanistic Experiments

Light Study

Light Source	Vial	SM (%)	TM (%)	Mass Balance (%)
Dark	borosilicate	85	0	85
Hood Light	borosilicate	73	0	73
23W CFL	borosilicate	25	25	50
Blue LED	**borosilicate**	**1**	**72**	**73**
UV Lamp	borosilicate	37	29	66
UV Lamp	quartz	24	33	57

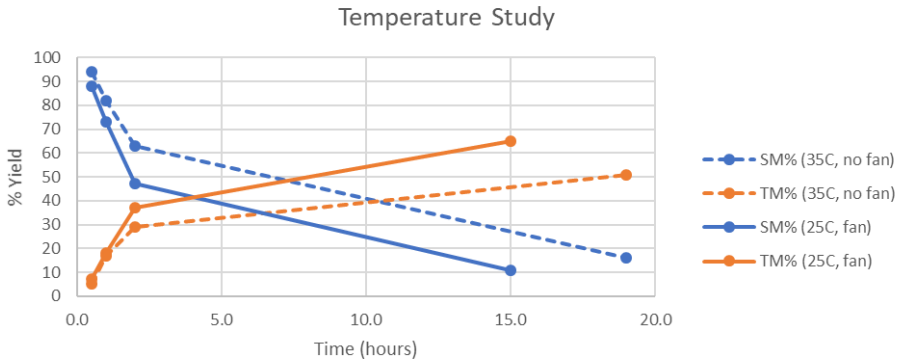
Reaction Conditions: 8-mL reaction vial, 0.0179 g (0.1 mmol) phenanthridine, 1 mL dichloromethane (DCM), 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 50 µL (0.4 mmol) 1-hexene, and 0.0809 g (0.4 mmol) diphenylphosphine oxide. All reagents combined in vial, under normal atmospheric conditions, and capped with a silicon septa pierced with a 18G, 1½"-long needle to allow air into the vial. Reaction vials placed 5.0 cm from lights for 43 hours. Isopropyl acetate was used as an internal standard to determine 1H NMR yields. Either one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue) were used for experiments moving forward.

Solvent Study with Phenanthridine



Reaction Conditions: 8-mL reaction vial, 0.0179 g (0.1 mmol) phenanthridine, 1 mL solvent, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial, under normal atmospheric conditions, and capped with a silicon septa pierced with a 18G 1½" needle to allow air into the vial. Reaction vials placed 5.0 cm from blue LED for 6.67 hours. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields.

Temperature Study



Reaction Conditions: 8-mL reaction vial, 0.0179 g (0.1 mmol) phenanthridine, 1 mL DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa pierced with a 18G 1½"-long needle to allow air into the vial. Reaction vials placed 5.0 cm from blue LED for stated time. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. Future reactions were conducted with a fan at room temperature.

Vial Headspace Study

Headspace	18G Needle	SM (%)	TM (%)	Mass Balance (%)
N2	N	55	21	76
Air	Y	20	64	84
Air	open top	20	11	31
Air	**N**	**19**	**70**	**89**
O2	Y w/O2 balloon	10	61	71
O2	N	17	49	66

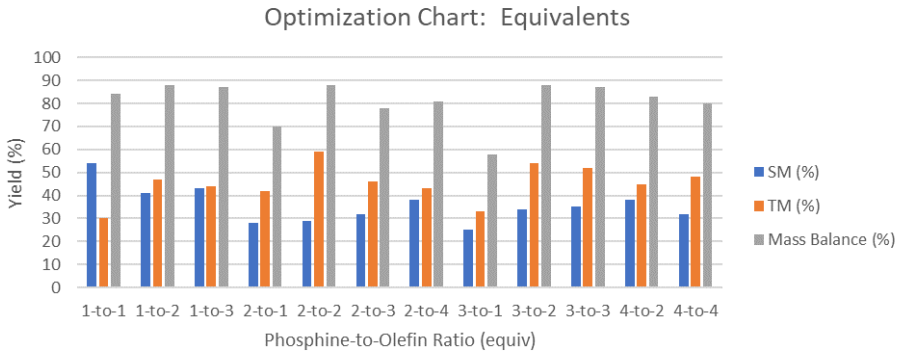
Reaction Conditions: 8-mL reaction vial, 0.0179 g (0.1 mmol) phenanthridine, 1 mL DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Some of the silicon septa were pierced with an 18G needle, open to air. Some reactions had atmosphere replaced with O2. Reaction vials placed 5.0 cm from blue LED for four hours. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. Future reactions were run with simple air atmosphere and a closed cap and septa to reduce the evaporation of reagents.

Concentration Study

Conc. (M)	DMSO (mL)	Rxn Vial Size	SM (%)	TM (%)	Mass Balance (%)
0.05	2.00	8-mL	34	55	89
0.05	2.00	20-mL	50	42	92
0.10	1.00	8-mL	19	59	78
0.10	**1.00**	**20-mL**	**3**	**69**	**72**
0.13	0.75	8-mL	18	55	73
0.13	**0.75**	**20-mL**	**3**	**71**	**74**
0.20	0.50	8-mL	20	60	80
0.20	0.50	20-mL	6	60	66

Reaction Conditions: 8-mL & 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, various volumes of DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Reaction vials placed 5.0 cm from blue LED for four hours. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. The 1-mL conditions were chosen due to improved solubility and ease of handling.

Reagent Ratio Study



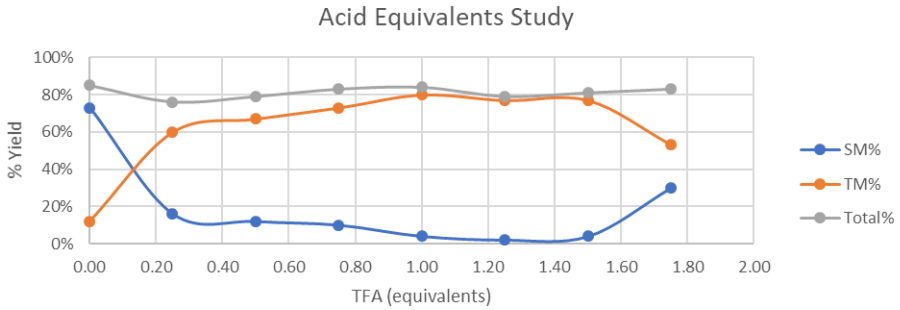
Reaction Conditions: 20-mL reaction vial, 0.0179 g (0.1 mmol) phenanthridine, 1 mL DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), various volumes (0.1-0.4 mmol) 1-hexene, and various masses (0.1-0.4 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Reaction vials placed 5.0 cm from blue LED for four hours. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. 2 equivalents of both olefin and secondary phosphine oxide were chosen as the optimal ratios.

DI Water Study

H2O Equiv	H2O Volume	SM (%)	TM (%)	Mass Balance (%)
0	0.0 uL	27	61	88
1	**1.8 uL**	**22**	**67**	**89**
10	**18 uL**	**25**	**68**	**93**
100	180 uL	66	32	98
1000	1.8 mL	96	4	100

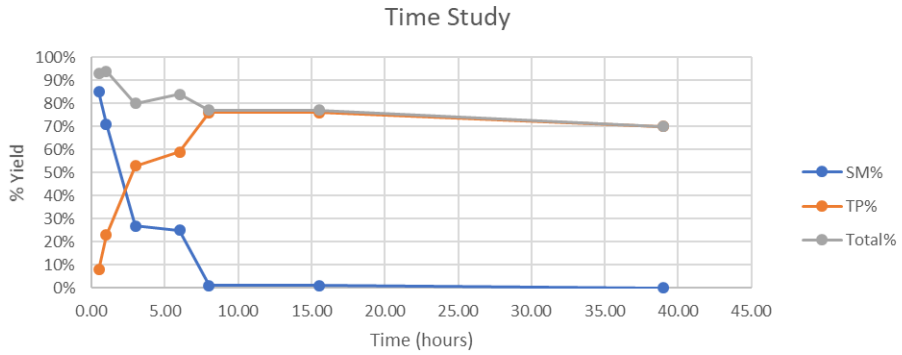
Reaction Conditions: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), various volumes of water, 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Reaction vials placed 5.0 cm from blue LED for four hours. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. It appears that the addition of DI water assist in the formation of product. 10 µL of water was chosen for future reactions.

Acid Study



Reaction Conditions: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, various volumes trifluoroacetic acid (TFA), 10 µL (0.55 mmol) water, 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Reaction vials placed 5.0 cm from blue LED for four hours. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. 1.2 equivalents of TFA were chosen as optimal.

Reaction Time Study



Reaction Conditions: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 10 µL (0.55 mmol) water, 25 µL (0.2 mmol) 1-hexene, and 0.0404 g (0.2 mmol) diphenylphosphine oxide. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. 12 hours (overnight) was chosen as optimal.

Initial Reaction Step Study of Hydrophosphorylation – 12 hours, various conditions

Conditions	Headspace	Starting Mat'l%	Target Mol. (%)	Mass Balance (%)
Control, no [Ir]	air	99	0	99
Added 0.1 mmol Na2CO3	air	0	76	76
normal	air	0	75	75
normal	N2	0	78	78

Reaction Conditions:

20-mL reaction vials, 1 mL of DMSO, 25 µL (0.2 mmol) 1-hexene, 0.0202 g (0.1 mmol) diphenylphosphine oxide, and 0.001 mmol of photocatalyst. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions or under nitrogen atmosphere after 3x freeze-pump-thaw, and capped with a silicon septa. Dibromomethane was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed 12 hours.

Photocatalyst Study with Pyridiniums – 12 hours, no water, no base

Photocatalyst	HP(O)Ph2 (%)	Hydrophos. (%)	reduced SM (%)	Starting Mat'l (%)	Target Mol (%)	Mass Balance (%)
Ir(ppy)2(dtbbpy)PF6	0	70	12	0	73	85
9-fluorenone	0	17	4	0	52	56
pyrylium	0	3	12	0	14	26
-	0	0	7	0	0	7

Reaction Conditions:

20-mL reaction vials, 0.0249 g (0.1 mmol) 1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.001 mmol of photocatalyst. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed 12 hours. Pyrylium used was 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate.

Photocatalyst Study with Pyridiniums – 7 hours, no water, no base

Photocatalyst	High O.S. Ox	Low O.S. Ox	HP(O)PH2 (%)	Hydrophos. (%)	reduced SM (%)	Target Mol (%)	Mass Balance (%)
$Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ (380nm)	+1.69 V	+1.21 V	0	36	16	72	88
$Ir(ppy)_2(dtbbpy)PF_6$ (380nm)	+0.66 V	+1.21 V	0	25	19	63	82
Eosin Y (539nm)	-	+0.79 V	20	18	14	46	60
Fluorescein (528nm)	-	+0.78 V	14	41	12	60	72
$Ru(bpy)_3PF_6$ (452nm)	+1.29 V	+0.77 V	50	5	20	12	32
fac-$Ir(ppy)_3$ (375nm)	+0.77 V	+0.31 V	8	16	56	22	78

Reaction Conditions:

20-mL reaction vials, 0.0249 g (0.1 mmol) 1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.001 mmol of photocatalyst. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dibromomethane was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed 7 hours.

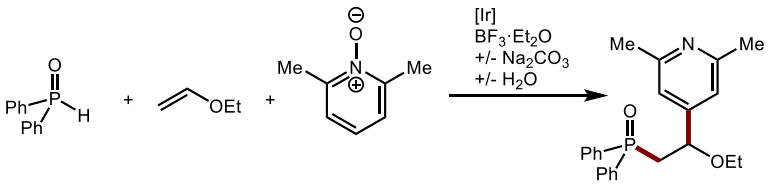
Photocatalyst Study with Pyridiniums – 12 hours, no base

Photocatalyst	High O.S. Ox	Low O.S. Ox	HP(O)PH2 (%)	Hydrophos. (%)	reduced SM (%)	Target Mol (%)	Mass Balance (%)
$Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$ (380nm)	+1.69 V	+1.21 V	0	50	9	71	80
$Ir(ppy)_2(dtbbpy)PF_6$ (380nm)	+0.66 V	+1.21 V	14	37	20	71	91

Reaction Conditions:

20-mL reaction vials, 0.0249 g (0.1 mmol) 1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate, 1 mL of DMSO, 10 µL (0.55 mmol) DI water, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.001 mmol of photocatalyst. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dibromomethane was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed 12 hours.

Activation of N-oxides with BF_3-etherate

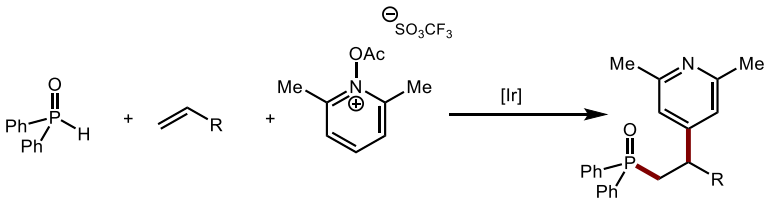


Conditions	N-oxide SM (%)	HP(O)Ph2 (%)	Hydrophos. (%)	2,6-lutidine (%)	Target Mol (%)	Mass Balance (%)
- Na2CO3, - H2O	57	0	12	15	0	72
+ Na2CO3, - H2O	48	0	9	13	4	65
+ Na2CO3, + H2O	50	20	21	14	0	64

Reaction Conditions:

20-mL reaction vials, 0.0123 g (0.1 mmol) 2,6-dimethylpyridine N-oxide, 1 mL of DMSO, +/- 10 µL (0.55 mmol) DI water, +/- 0.0106 g (0.1 mmol) sodium carbonate, 19 µL (0.2 mmol) ethyl vinyl ether, 0.025 mL (0.2 mmol) of BF_3-etherate, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.0009 g (0.001 mmol) of photocatalyst ($Ir(ppy)_2(dtbbpy)PF_6$). All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dichloroethane was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed 6 hours. Regardless of conditions tested, a majority of the mass balance was the N-oxide starting material. Minor reduction of the N-oxide was observed in all three cases, leading to 2,6-lutidine accounting for 13-15% of the total mass. Finally, only 4% of the desired product was observed in the reaction condition where base was used but water was not added. Other activation strategies were investigated for pyridines.

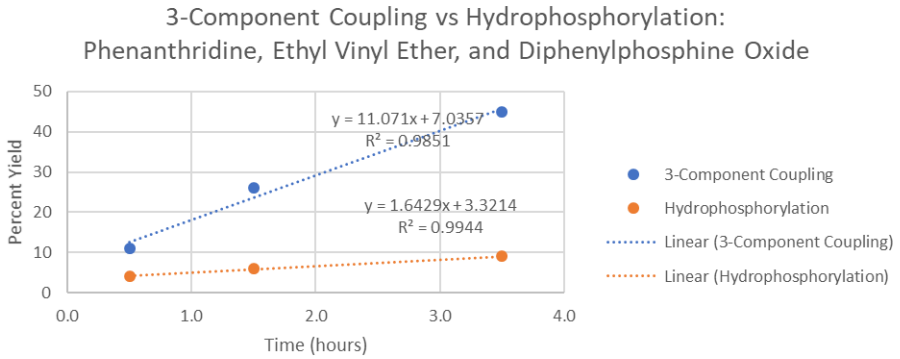
Activation via 1-Acetoxypyridin-1-ium



Alkene (R)	Starting Mat'l (%)	HP(O)Ph2 (%)	Hydrophos. (%)	2,6-Lutidine (%)	Target Mol. (%)	Phos-Hetero. (%)	Mass Balance (%)
1-hexene (nBu)	0	0	0	63	0	35	98
ethyl vinyl ether (OEt)	0	0	5	60	0	35	95

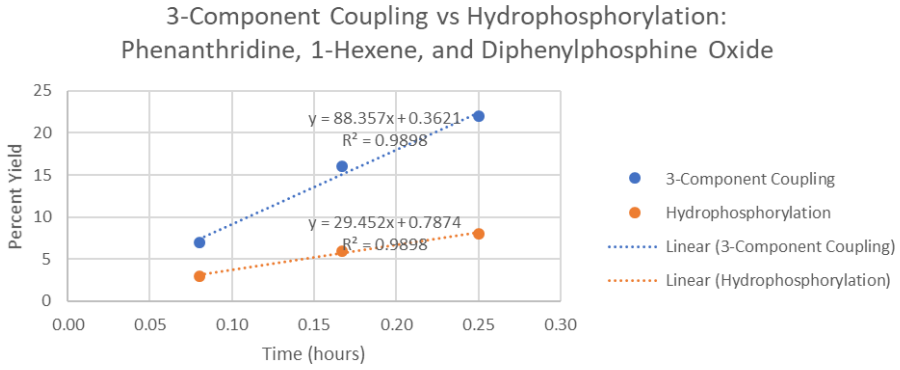
20-mL reaction vials, 0.0315 g (0.1 mmol) 1-acetoxy-2,6-dimethylpyridin-1-ium trifluoromethane sulfonate, 1 mL of DMSO, 0.0106 g (0.1 mmol) sodium carbonate, 25 µL (0.2 mmol) 1-hexene or 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.0009 g (0.001 mmol) of photocatalyst ($Ir(ppy)_2(dtbbpy)PF_6$). All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dichloroethane was used as an internal standard to determine ^1H NMR yields. Reaction was allowed to proceed 12 hours. Regardless of alkene tested, a majority of the mass balance was the direct reduction of the starting material leading to 2,6-lutidine accounting for 60-63% of the total mass. Finally, although not isolated, it appears as if the direct phosphorylation of the pyridine resulted in 35% of the mass balance. Because no target molecule was found and because of the large amount of direct reduction of the starting acetoxypyridinium observed, other activation strategies were investigated for pyridines.

3-Component Coupling versus Hydrophosphorylation



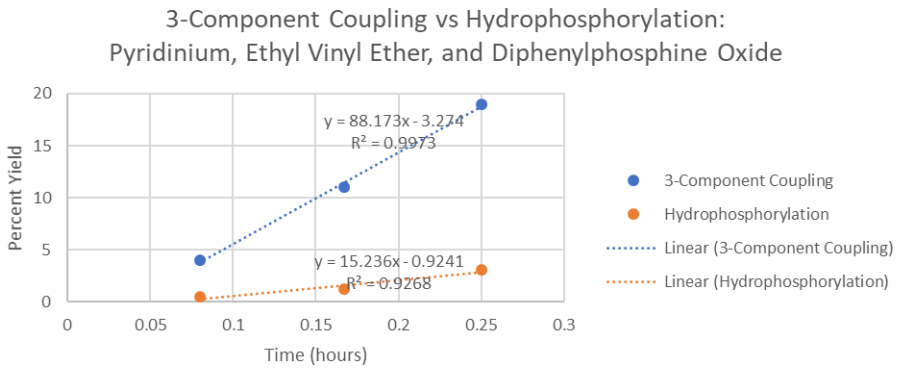
Reaction Conditions:

Phenanthridine, Ethyl Vinyl Ether, & Diphenylphosphine Oxide: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 9.5 µL (0.1 mmol) ethyl vinyl ether, 0.0202 g (0.1 mmol) diphenylphosphine oxide, and 0.0009 mmol of $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dibromomethane was used as an internal standard to determine ^1H NMR yields. Reaction was allowed to proceed 0.5, 1.5, and 3.5 hours. 3-Component Coupling appears to be about 6.7 times faster than Hydrophosphorylation under these conditions.



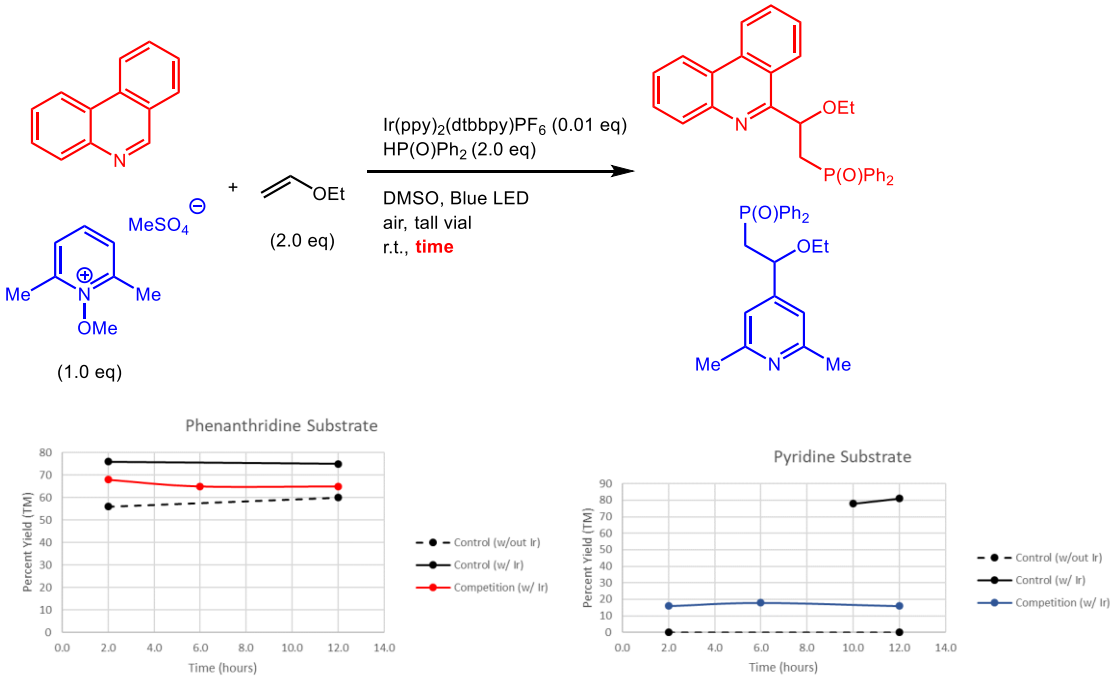
Phenanthridine, 1-Hexene, & Diphenylphosphine Oxide: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 9.2 µL (0.12 mmol) trifluoroacetic acid (TFA), 10 µL (0.55 mmol) water, 12.5 µL (0.1 mmol) 1-hexene, 0.0202 g (0.1 mmol) diphenylphosphine oxide, and 0.0009 mmol of $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with

magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dibromomethane was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed 0.5, 1.5, and 3.5 hours. 3-Component Coupling appears to be about 3.0 times faster than Hydrophosphorylation under these conditions.



<u>1-Methoxy-2,6-dimethylpyridin-1-ium Methylsulfate, Ethyl Vinyl Ether, & Diphenylphosphine Oxide:</u> 20-mL reaction vials, 0.0249 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 10 µL (0.55 mmol) of DI water, 9.5 µL (0.1 mmol) ethyl vinyl ether, 0.0202 g (0.1 mmol) diphenylphosphine oxide, and 0.0009 mmol of $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Dibromomethane was used as an internal standard to determine ^{1}H NMR yields. Reaction was allowed to proceed for 5, 10, and 15 minutes. 3-Component Coupling appears to be about 5.8 times faster than Hydrophosphorylation under these conditions.

Competition Study Between Phenanthridine and Pyridinium Methylsulfate



Reaction Conditions – Controls

Phenanthridine Control w/ Ir photocatalyst: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.0009 g of $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^1H NMR yields. Time points at 2 and 12 hours were taken.

Phenanthridine Control w/out Ir photocatalyst: 20-mL reaction vials, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, without $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^1H NMR yields. Time points at 2 and 12 hours were taken.

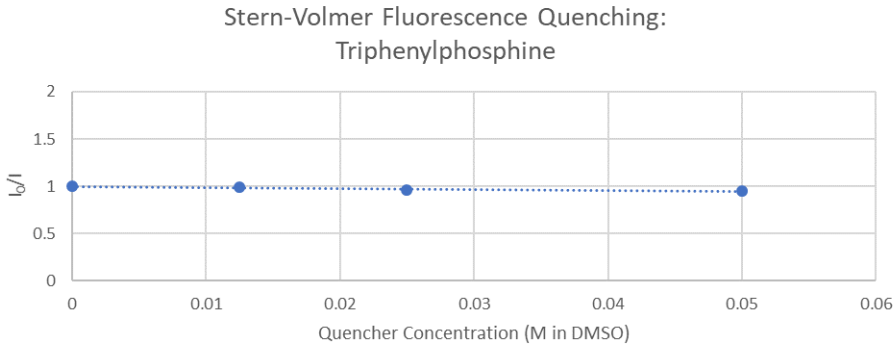
Pyridinium Control w/ Ir photocatalyst: 20-mL reaction vials, 0.0249 g (0.1 mmol) 1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.0009 g of $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^1H NMR yields. Time points at 10 and 12 hours were taken.

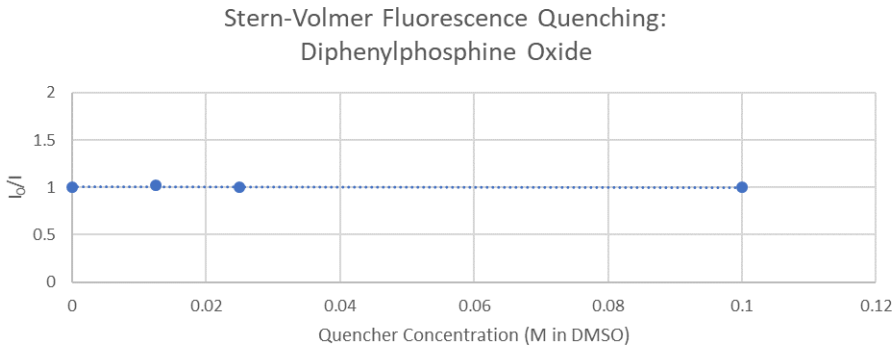
Pyridinium Control w/out Ir photocatalyst: 20-mL reaction vials, 0.0249 g (0.1 mmol) 1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, without $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^1H NMR yields. Time points at 2 and 12 hours were taken.

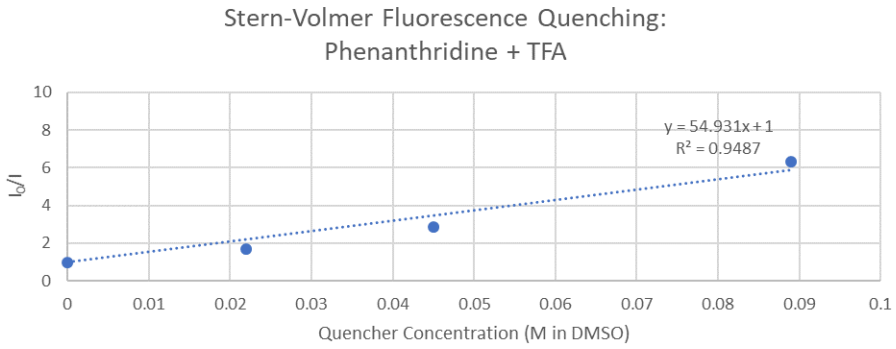
Reaction Conditions – Competition

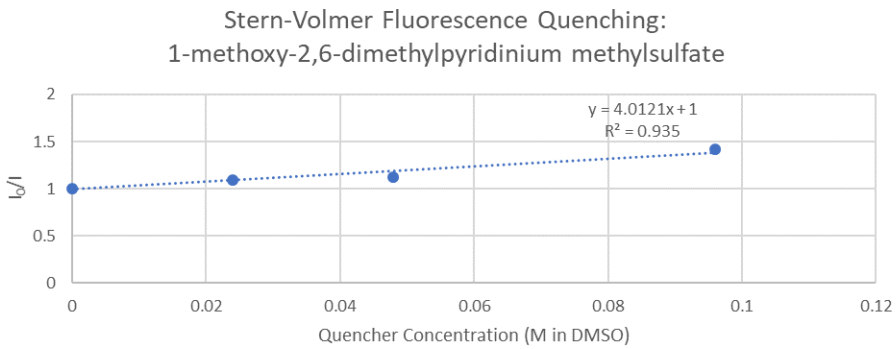
Competition Reactions w/ Ir photocatalyst: 20-mL reaction vials, 0.0249 g (0.1 mmol) 1-methoxy-2,6-dimethylpyridin-1-ium methyl sulfate, 0.0179 g (0.1 mmol) phenanthridine, 1 mL of DMSO, 19 µL (0.2 mmol) ethyl vinyl ether, 0.0404 g (0.2 mmol) diphenylphosphine oxide, and 0.0009 g of $Ir(ppy)_2(dtbbpy)PF_6$. All reagents combined in vial equipped with magnetic stir bar, under normal atmospheric conditions, and capped with a silicon septa. Isopropyl acetate was used as an internal standard to determine ^1H NMR yields. Time points at 2, 6, and 12 hours were taken.

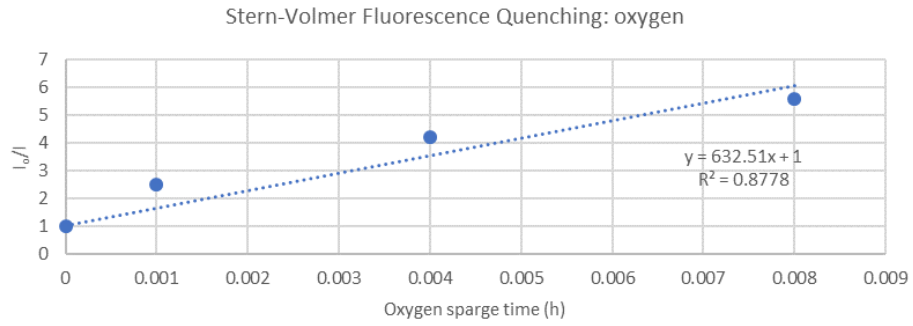
Stern-Volmer Fluorescence Quenching Studies











Conditions: (a) Reagent aliquots were taken from degassed stock solutions in glovebox under nitrogen atmosphere, mixed together, and then capped. Fluorescence values were determined using a Agilent Cary Eclipse Fluorescence Spectrophotometer and values are averages of three separate data points. (b) O_2-quenching: The iridium photocatalyst (1mg, 0.001 mmol) was added to a vial in a glovebox under nitrogen atmosphere, mixed with DMSO (3 ml), and then capped. During the experiment, O_2 was bubbled through the sample over time and analyzed. The quenching constant (K_{SV} = 633) is presumed to be a lower limit since concentrations (0.1 M) attained in other quenching studies were not achieved.

VI. References

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